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CCCLXXVI.—*The Heat of Combustion of Salicylic Acid.*

By Endre Berner.

Benzoic acid, naphthalene, and sucrose are the substances generally used for the determination of the heat capacity of a bomb calorimeter. A number of recent excellent investigations have shown, however, that only benzoic acid fulfils the requirements of a calorimetric standard. This acid, therefore, has been accepted as the sole standard substance for calorimetric work; its heat of combustion has been fixed at 6324 calories (15°) per gram weighed in air or 6319 calories (15°) per gram (vac.) ("Comptes Rendus de la Troisième Conférence Internationale de la Chimie," Lyon, 1922, p. 54).

International acceptance of one or more other substances as secondary standards is highly desirable, because the use of a single substance involves a certain risk of introducing an error in the value of the heat capacity of a calorimeter.

Verkade and Coops (*Rec. trav. chim.*, 1924, **43**, 561) recently proposed salicylic acid as a secondary standard substance. They determined its heat of combustion and tested its applicability as a thermochemical standard, but, unfortunately, they failed to take the precautions necessary to secure the utmost purity of their samples.

The author has now determined the heat of combustion of the pure acid. Three different preparations of salicylic acid (Merck, Kahlbaum, and von Heyden) were separately purified, partly by crystallisation from different solvents and partly by sublimation in a vacuum, until the heats of combustion of the products were constant; the values obtained, 5233·8, 5233·8, and 5233·9 cal. (15°) per gram (vac.), were identical within the limits of experimental error.

From the results of twenty experiments made with these samples, the mean value 5233·8 cal. (15)° per gram (vac.) was found for the heat of combustion of salicylic acid at constant volume. To this corresponds the value 5237·4 cal. (15°) per gram weighed in air against brass weights. The ratio of the heats of combustion of benzoic acid and salicylic acid is $6319/5233{\cdot}8 = 1{\cdot}2073$ (vac.).

Verkade and Coops (*loc. cit.*, p. 571) found a slightly higher value for the heat of combustion of salicylic acid, *viz.*, 5238 cal. (15°) per gram (vac.), and consequently the ratio 1·2066. The discrepancy may be due to an error in the heat capacities of the calorimeters or to a difference in purity of the acids. The first explanation is highly improbable, because both Verkade and Coops and the author used

benzoic acid from the Bureau of Standards, Washington, for the calibration of their calorimeters and obtained almost the same value [V. and C., 5238·1 ; B., 5237·1 cal. (15°) per gram (vac.)] for the heat of combustion of Merck's salicylic acid (" Präparate von bestimmter Verbrennungswärme "). Verkade and Coops used salicylic acid from four different sources. Because the heats of combustion of those preparations all agreed and one of them—Merck's—gave the same value after a single recrystallisation from ether, the authors contend that their preparations were " absolutely pure." These facts, however, are of no practical value as proofs of the purity of their preparations.

The combustion of salicylic acid (about 0·80 g.) in oxygen at a pressure of 35, 30, or 25 atmospheres is complete; neither carbon monoxide nor the slightest trace of soot nor any smell due to products of incomplete combustion can be detected. Moreover, the acid is neither hygroscopic nor volatile and is easily pressed into pellets which ignite readily. It should therefore be particularly suitable as a standard substance for calorimetric work.

Experimental.

Detailed descriptions of the calorimeter, the method and the experimental results will be published elsewhere.

The calorimeter was of the form recommended by the Bureau of Standards, Washington (*Bull.*, 1915, **11**, 189).

The calorimetric bomb had a thick fixed gold lining and a capacity of about 300 c.c.

Temperature measurements were made with a platinum resistance thermometer. The resistance was measured by Kohlrausch's method (" uebergreifende Nebenschlüsse ") as used by Jaeger and von Steinwehr (*Ann. Physik*, 1906, **21**, 23) and by Fischer and Wrede (*Sitzungsber. Preuss. Akad. Wiss. Berlin*, 1908, **5**, 129).

The cooling correction, u', was calculated from the formula

$$u' = a\int_{t_1}^{t_2} (u - u_0)dt,$$

in which a is the constant of the calorimeter, u its temperature, u_0 the convergence temperature, and t_1 and t_2, respectively, the time at the beginning and the end of the main period. The numerical value of the integral was in every case determined graphically. In some cases, the cooling correction was also computed by the practical method developed by Dickinson of the Bureau of Standards (*loc. cit.*, p. 229). This method gave practically the same values as those obtained by the complete computation and therefore may be used even in work of high precision.

The total rise of temperature during a combustion was about

1°. The temperature of the jacket was always regulated so that the cooling correction amounted to 2—3 parts in 1000.

The oxygen was prepared from liquid air; it contained very little nitrogen—the correction for nitric acid was 0·5—0·7 cal.—and no combustible impurities. Oxygen from the same source was used for the calibration of the calorimeter and for the combustion of the salicylic acid.

Ignition of the substance was effected electrically by means of a very thin platinum wire; the heat developed by the current was about 0·8 cal. If the wire had been merely pressed into the pellet, ignition sometimes failed to occur. A part of the wire was therefore covered with 0·5—1·5 mg. of benzoic acid by dipping it in the molten acid and placed close against the top of the pellet; under these conditions ignition never failed to take place.

Heat Capacity of the Calorimeter.—This was determined by the combustion of two samples of benzoic acid, (*a*) a standard sample (39b) obtained from the Bureau of Standards, Washington, and (*b*) a sample (517) purified as follows: Benzoic acid (Kahlbaum's "Präparate für kalorimetrische Bestimmungen") was distilled twice at a pressure of 10 mm. of Hg, crystallised twice from benzene and once from carbon disulphide, finely powdered, and dried for 3 days in a vacuum over phosphorus pentoxide.

With 3700 g. of water in the calorimeter vessel, 1 g. of water in the bomb, and an oxygen pressure of 30 atmospheres, the heat capacity was found to be 4066·3 calories (15°) at a mean temperature of 18°. To this value must be added a small correction for the difference in heat capacity of the products of combustion and the oxygen necessary for the combustion. In some recent experiments, the variation of the heat capacity with temperature was determined directly; the heat capacity decreased by about 1 cal. for an increase of 1° at 18°. If the mean temperature during an experiment differed from 18°, a correction for the divergence was applied.

Purification of the Salicylic Acid.—1. Merck's salicylic acid ("Präparate von bestimmter Verbrennungswärme") was finely powdered and dried for 3 days in the way described above (sample 571).

The same preparation was crystallised twice from water and once from chloroform, powdered, and dried for 3 days (sample 571 IIa). It was then dried for 6 days (sample 571 IIb), and sublimed in a vacuum (sample 571 III).

2. Salicylic acid (Kahlbaum D.A.B.5) was crystallised once from water sublimed in a vacuum, crystallised once from chloroform, powdered and dried for 3 days (sample 572 III). This sample was then crystallised once from water, once from benzene, and

once from chloroform, powdered, and dried for 3 days (sample 572 IV).

3. Salicylic acid (von Heyden's "Acidum Salicylicum volum. puriss.") was crystallised twice from water and once from chloroform and dried for 3 days (sample 573 II). This sample was crystallised once from water, once from chloroform, and dried for 3 days (sample 573 III).

TABLE I.

Benzoic Acid.

p = pressure of oxygen in atms.; h = heat capacity, in cal. (15°), of the calorimeter at 18° and 30 atms. of oxygen; d = deviation from the mean heat capacity in parts per 10,000.

Sample.	p.	h.	d.	Sample.	p.	h.	d.
39*b*	30	4066·7	+1·0	517	40	4066·6	+0·7
,,	,,	4065·6	−1·7	,,	30	4065·8	−1·2
,,	,,	4066·7	+1·0	,,	,,	4066·6	+0·7
,,	35	4065·2	−2·7	,,	,,	4066·2	−0·2
517	30	4066·9	+1·5	,,	,,	4066·9	+1·5
					Mean	4066·3	

TABLE II.

Salicylic Acid.

p = Pressure of oxygen = 35 atms.; t = mean temperature; Q = heat of combustion per gram (vac.) in cal (15°); D = deviation from mean heat of combustion in parts per 10,000.

Salicylic acid (Merck).

Sample.	t.	Q.	D.
571	18·0°	5237·3	+0·4
,,	18·3	5237·3	+0·4
,,	18·0	5236·4	−1·3
,,	18·1	5237·0	−0·2
,,	18·1	5237·3	+0·4
	Mean	5237·1	

Salicylic acid (von Heyden), purified.

Sample.	t.	Q.	D.
573 II	18·8°	5234·3	+0·8
,,	17·9	5233·1	−1·5
573 III	18·0	5234·4	+1·0
,,	17·9	5234·7	+1·5
,,	18·0	5233·2	−1·3
	Mean	5233·9	

Salicylic acid (Merck), purified.

571 IIa	18·1°	5234·6	+1·5
,,	18·1	5233·3	−1·0
571 IIb	18·2	5233·3	−1·0
,, *	18·1	5233·9	+0·2
,, †	18·0	5232·9	−1·7
571 III	18·1	5234·5	+1·3
,,	18·0	5233·1	−1·3
,,	18·0	5234·4	+1·1
	Mean	5233·8	

Salicylic acid (Kahlbaum), purified.

572 III	18·2°	5234·1	+0·6
,,	18·2	5233·3	−1·0
,,	18·1	5234·1	+0·6
572 IV	18·5	5233·7	−0·2
,,	18·5	5234·6	+1·5
,,	17·9	5233·0	−1·5
,,	18·0	5233·7	−0·2
	Mean	5233·8	

* p = 30 atms. † p = 25 atms.

NORGES TEKNISKE HÖISKOLE,
TRONDHJEM, NORWAY.

[*Received, July 9th*, 1925.]

CCCLXXVII.—*Unstable States of Solutions of Sodium Behenate.*

By Mary Evelyn Laing.

Previous communications from this laboratory were devoted to describing the most stable forms of soap and its solutions. In the case of sodium behenate, it was incidentally noted that the type of solution obtained could be radically affected by suitable treatment. For example, on repeated rapid cooling, the behenate solutions could be obtained at room temperature for a short period as limpid, mobile liquids, whereas slow cooling produced the usual hard, white curd. Reheating the mobile liquid of a $0{\cdot}2N_w$-solution to about 90° produced a clear, stiff, isotropic jelly, which quick cooling once more temporarily rendered fluid. Some of the most interesting solutions could only be kept less than half an hour.

The appearance and behaviour of these solutions and their transitory states have been quantitatively examined.

The task was undertaken by a team of experienced investigators, who worked simultaneously on portions of solutions prepared by Mr. G. M. Langdon. He also made the macroscopic observations. The microscopic study was undertaken by Mr. S. E. Wiltshire, Miss M. E. Kieser carried out the *E.M.F.* experiments, Miss M. E. Laing the freezing-point determinations, Miss K. M. Hay the indicator tests, and Mr. W. C. Quick measured the conductivity.

Sodium behenate solutions were made up in silver tubes by shaking the requisite quantities (Bunbury and Martin, J., 1914, **105**, 417) of standardised alkali with weighed quantities of behenic acid, m. p. 81·0—82·0°, kindly made for us by Messrs. J. C. Crosfield and Sons, Ltd., by the catalytic hydrogenation of Kahlbaum's erucic acid. The homogeneous soaps were transferred to thick-walled glass tubes, which were sealed for optical investigation according to the method previously described (McBain and Langdon, this vol., p. 852). Parallel experiments were carried out with solutions made up in 1913 (McBain and Taylor, *Z. physikal. Chem.*, 1911, **76**, 179). The strengths used were 0·01, 0·05, 0·1, 0·2, $0{\cdot}5N_w$, *i.e.*, mole per 1000 g. of water. The observations here recorded were repeated many times; *e.g.*, a $0{\cdot}1N_w$-solution was alternately heated and cooled twenty times under different conditions and the results were reproducible, the only effect that varied being the number of "flocks" appearing in the mobile liquid.

The stable forms of the behenate solutions at room temperature, with the exception of $0{\cdot}01N_w$, were solid, white, moist curds. Curd formation, however, could be suspended by special heat treatment,

as was well illustrated by the behaviour of a $0{\cdot}05N_w$-solution. On being heated to about 88°, the curded $0{\cdot}05N_w$-solution melted to a fairly mobile, milky liquid containing a few white flakes. If this solution were allowed to cool slowly, more flakes separated and the whole gradually became a network of curd; the transformation from Brownian particles in movement to short and then long fibres could be observed under the ultramicroscope. Photographs of such gradual transitions have been published elsewhere (McBain, Darke, and Salmon, *Proc. Roy. Soc.*, 1921, *A*, **98**, 395; Bogue, "Colloidal Behaviour," Vol. I, pp. 410—429; *Nature*, 1921, **107**, 45; Alexander, "Colloid Chemistry, Theoretical and Applied," Vol. I, 1925).

On cooling rapidly, the white flakes, which formed at about 75°, rose to the surface, leaving a clear lower layer. On heating to 90°, these flakes melted and the system consisted of two clear layers. As the tube cooled again, curding took place in two stages, the upper layer solidifying at 75° and the clear lower layer after some hours at room temperature.

The quantitative investigation had to be carried out as quickly as possible, before the homogeneous, mobile liquid produced by rapid cooling set to a mass of curd fibres.

The hydroxyl-ion concentration of the $0{\cdot}05N_w$-solution at 18° was found by *E.M.F.* measurements with the hydrogen electrode to be $0{\cdot}007N_w$ during the first hour, but this value declined to $0{\cdot}0008N_w$ when the clear liquid had solidified to form white curd. The concentration of hydroxyl ions in the mobile liquid was shown by the indicator method, using alizarin yellow G and Sörensen's buffers, to be $0{\cdot}007N_w$ at 90° and slightly higher at room temperature.

The clear $0{\cdot}05N_w$-sodium behenate at 18°, therefore, is hydrolysed to the extent of 14% (= $0{\cdot}007N_w$-OH) and contains $0{\cdot}021N_w$-acid soap expressed in terms of behenate, or $0{\cdot}014N_w$, in terms of sodium; if this is formed, as in the case of the palmitate, according to the equation $3\text{NaBe} + \text{H}_2\text{O} = \text{NaOH} + 2\text{NaBe,HBe}$. Hence 42% of the total behenate radical is in the form of acid soap. This acid soap is colloidal and exerts no osmotic pressure (McBain, Taylor, and Laing, J., 1922, **121**, 621).

The osmotic data were obtained from depressions of the freezing point, determined by the usual Beckmann method, using inoculation; at least four concordant readings were taken before a solution curded. The depression for the $0{\cdot}05N_w$-solution was 0·036°. The hydroxyl ions, present to the extent given above, would correspond to a depression of 0·013° and together with the equivalent sodium ions would account for a depression of 0·026°. The difference, 0·010°, which must be due to that part of the soap in solution as electrolyte, corresponds to 0·0027 g.-mol. of fully dissociated, binary, crystal-

loidal electrolyte. What remains of the total concentration $0{\cdot}05 - 0{\cdot}014 - 0{\cdot}007 - 0{\cdot}0027N_w = 0{\cdot}0263N_w$, must be the concentration of the undissociated neutral colloid. The constituents of this unstable but clear solution, and their concentrations, are very nearly those in Table I.

TABLE I.

Constituents of unstable $0{\cdot}05N_w$-Sodium Behenate at 18°.

1. From *E.M.F.* (OH′)	$0{\cdot}007N_w$		14% hydrolysis alkalinity.
2. Equivalent to Na_2HBe_3	$0{\cdot}0140N_w$	(Na·)	42% acid soap (colloid).
3. From lowering (Na·)=(Be′)+(OH′)	$0{\cdot}0097N_w$		5% dissociated soap.
4. Remainder $(NaBe)_2$	$0{\cdot}0263N_w$	(Na)	53% neutral colloid.

The conductivity data are summarised in Table II. The conductivities of two samples of $0{\cdot}05N_w$-solution were measured at intervals over a period of 20 hours, and that of a $0{\cdot}1N_w$-solution at intervals during 18 hours, after making up. The values recorded for the liquid are the means of those obtained within the first hour, the curd values are those obtained after 18—20 hours.

TABLE II.

Specific Conductivity (κ) of Sodium Behenate Solutions at 18°.

	Unstable liquid.		Final curd.	
Conc. (N_w).	κ.	α%.	κ.	α%.
0·05	$1{\cdot}74 \times 10^{-3}$	15·9	$0{\cdot}311 \times 10^{-3}$	2·8
0·1	$2{\cdot}79 \times 10^{-3}$	12·8	$0{\cdot}42 \times 10^{-3}$	1·9

The degree of dissociation, α, calculated by dividing the actual conductivity found by the molar conductivity of sodium hydroxide at infinite dilution at 18° (*viz.*, 216·5) is 15·9% for the $0{\cdot}05N_w$-solution, a value slightly greater than that (14%) found by *E.M.F.* measurements; the approximate agreement shows that the free hydroxide accounts for most of the conductivity. A more exact comparison may be made by calculating from the data of Table I the specific conductivity of the $0{\cdot}05N_w$-solution at 18°. The products of the concentrations per c.c. of the various ions shown in Table I and their respective mobilities (43·6 for Na·, 172·9 for OH′, and 20·7 for Be′) being added together, the calculated value for the specific conductivity is found to be $1{\cdot}69 \times 10^{-3}$. The agreement with the observed value, $1{\cdot}74 \times 10^{-3}$, is very close, especially in view of the fact that different samples of unstable solutions were taken for these measurements; one sample actually gave the value $1{\cdot}69 \times 10^{-3}$ reciprocal ohm.

Full allowance having been made for the conductivity due to the hydroxyl ions in the final curd, it is evident that the curd fibres, though not in solution (this was shown by analysis of the mother-

liquor squeezed out from such curds), contribute to the residual conductivity. This is apparently due to the free ions of the electrical double layer of the very extensive surface of the fine fibres (compare Laing, *J. Physical Chem.*, 1924, **28**, 673; Laing and McBain, J., 1920, **117**, 1507). The data show that these supercooled solutions are highly unstable, the extent of hydrolysis being many times greater even than that for the solutions at 90°. At the lower temperature, after a short time, the hydrolysis diminishes to a tenth of its value and the equilibrium shifts in favour of the formation of insoluble sodium behenate, which separates in curd form from the solution. It seems possible that in the initial clear liquid the acid soap may peptise the neutral soap. Solutions of acid soap froth freely (McBain, Taylor, and Laing, *loc. cit.*).

The $0{\cdot}1N_w$-behenate solution in the unstable condition was similar to the $0{\cdot}05N_w$-solution, but was less hydrolysed. The concentration of hydroxyl ions due to hydrolysis was shown by the hydrogen electrode to be $0{\cdot}0098N_w$ or 9·8% (afterwards falling to $0{\cdot}0012N_w$ when the clear liquid had set to a white curd). The depression of the freezing point was 0·035°. This would be fully accounted for by the free sodium hydroxide, but, as is seen from Table II, there is still a small amount of conductivity to be accounted for as in the case of the $0{\cdot}05N_w$-solution.

The macroscopic and the microscopic behaviour of the $0{\cdot}1N_w$-solution are just like those of the $0{\cdot}05N_w$-solution described above, except that the instability increases with concentration.

The $0{\cdot}2N_w$-solution was too unstable to permit of freezing-point determinations. This solution is very viscous and difficult to prepare. It exhibited, however, a remarkable change in viscosity. The melted curd was a clear, isotropic jelly at 90°, but, on cooling, the gel " melted " to a mobile, cloudy liquid. We have observed this curious phenomenon of gelation at a relatively high temperature and fluidity at a low temperature in only one other instance, namely, in a solution of nitro-cotton in alcohol; this is a clear, elastic jelly at room temperature and a mobile fluid at the temperature of liquid air (observation by Mr. L. E. Smith in this laboratory).* This observation can be readily explained on the basis of the theory of neutral colloids put forward by McBain (*Trans. Faraday Soc.*, 1924, **20**, 22).

The hydroxyl-ion concentration of the $0{\cdot}2N_w$-solution is $0{\cdot}005N_w$, indicating a hydrolysis alkalinity of only 2%. This value corresponds exactly with that found by the indicator method. Most of the soap of the $0{\cdot}2N_w$-solution must be present as insoluble, undissociated, neutral colloid.

* Compare Szegvari (*Kolloid-Ztg.*, 1924, **34**, 34), who, however, used a more complicated mixture of solvent and non-solvent.

Whether cooled rapidly or slowly, the $0{\cdot}5N_w$-solution of sodium behenate forms curd at room temperature. It is a highly viscous gel at 90°.

It appears that ease of curding increases with rise of viscosity, which takes place whenever separated matter (shown by streakiness) is present, or upon lowering of temperature. Curd also forms more rapidly after the solution has been heated in glass.

A sodium behenate solution separates into two layers on addition of $0{\cdot}4N_w$-sodium chloride; whereas in the case of sodium palmitate of the same concentration, twice this quantity of salt is required to produce the same change. The salted-out system, $0{\cdot}05\ N_w$-NaBe + $0{\cdot}42N_w$-NaCl, and also $0{\cdot}05N_w$-NaBe + $0{\cdot}59N_w$-NaCl, becomes homogeneous at 100°. This temperature is above that, 72—75°, at which the corresponding palmitate–sodium chloride system becomes homogeneous. Both facts are in accordance with the insolubility of sodium behenate at low temperatures.

Neutral behenate solutions, in the absence of sodium chloride, were never observed to separate spontaneously into two layers on standing at high temperatures, as is the case with acid sodium palmitate ($0{\cdot}4N_w$-NaP, $0{\cdot}1N_w$-HP). In appearance, the acid salts of behenic and palmitic acids are very similar.

On reviewing the behaviour of these colloidal behenate systems, one is struck by their analogy with certain crystalloidal systems. When, for example, barium sulphate is produced rapidly from a mixture of barium chloride and a sulphate, a highly supersaturated solution may be obtained which deposits matter in the colloidal state. On sudden cooling of the behenate solutions, supersaturation with respect to neutral colloid sets in and similar amorphous, flocculent material is formed. Thus on cooling of either system, colloid or crystalloidal, one gets separation of (crystalline) curd fibres on the one hand and of true crystals on the other. On standing in contact with their respective mother-liquors, colloidal barium sulphate crystallises and colloidal sodium behenate curds.

Summary.

(1) Although the stable form of $0{\cdot}05$—$0{\cdot}5N_w$-sodium behenate at room temperature is a hard, white curd, these solutions can be obtained temporarily as clear, very mobile liquids, which are hydrolysed to an abnormally large extent.

(2) The largest constituent of the unstable mobile solutions is neutral undissociated colloid, the next largest being colloidal acid sodium soap with the equivalent quantity of free sodium hydroxide. There is only a very small proportion of dissociated soap.

UNIVERSITY OF BRISTOL. [*Received, July 24th*, 1925.]

CCCLXXVIII.—*Sulphur Compounds Removed from a Persian Petroleum by Means of Sulphuric Acid. Part I.*

By Edward Henry Thierry.

Mabery and Smith (*Amer. Chem. J.*, 1891, **13**, 232) isolated several organic sulphur compounds from a crude Ohio oil and established the presence of a series of dialkyl sulphides. Mabery and Quayle (*ibid.*, 1906, **35**, 404) obtained very different results during an investigation of a Canadian petroleum, a series of saturated cyclic compounds, named thiophanes, of the empirical composition $C_nH_{2n}S$ being isolated; the actual compounds ranged from $C_7H_{14}S$ to $C_{18}H_{36}S$ and a derivative of the substance $C_6H_{12}S$ also was prepared (see also von Braun and Trümpler, *Ber.*, 1910, **43**, 543; Trochimovski, *J. Russ. Phys. Chem. Soc.*, 1916, **48**, 880). More recently, other workers have described the isolation and identification of thiophen and its homologues in shale oil.

The product now investigated was a sulphuric acid sludge from the refining of Persian petroleum kindly supplied by Mr. Kewley of the Asiatic Petroleum Co. The oil that separated on dilution was carefully fractionated and of the twenty-nine fractions boiling below 120°/125 mm., four have been investigated. Three of these consisted essentially of methyl ethyl sulphide, tetra- and pentamethylene sulphides. The fourth fraction was a mixture. It contained a compound $C_4H_{10}S$; this was not diethyl sulphide, but sufficient material was not available to determine whether it was methyl propyl sulphide or methyl *iso*propyl sulphide. All the fractions had an intense odour, but the purest samples of the cyclic sulphides were in no sense objectionable. The various compounds have been characterised by the preparation of a number of derivatives such as sulphonium iodides and double salts with mercuric salts.

Experimental.

The dark supernatant oil obtained by greatly diluting the sulphuric acid sludge (12 litres) with water was shaken with sodium hydroxide and dried over sodium sulphate; a further quantity was extracted from the diluted liquid with chloroform, the total yield being 1800 c.c. The oil was distilled and the more volatile portions were fractionated five times at a pressure of 760 mm.; the fractions obtained were: (1) below 50°, 0·5 c.c.; (2) 59—64°, 90 c.c.; (3) 64—68°, 11 c.c.; (4) 68—70°, 23 c.c.; (5) 70—80°, 10 c.c.; (6) 80—89°, 8 c.c.; (7) 89—92°, 11 c.c.; (8) above 92°, 7 c.c.

The oils boiling above 100°/760 mm. were fractionated eleven times at 125 mm. Table I shows the degree of separation achieved.

TABLE I.

Fraction.	B.p./125 mm.	C.c.	Fraction.	B.p./125 mm.	C.c.
9	up to 60°	4	20	90—93°	30
10	60—63	12	21	93—96	12
11	63—66	20	22	96—99	9
12	66—69	3	23	99—102	19
13	69—72	5	24	102—105	28
14	72—75	5	25	105—108	16
15	75—78	10	26	108—111	14
16	78—81	70	27	111—114	35
17	81—84	75	28	114—117	20
18	84—87	10	29	117—120	18
19	87—90	3	Residue (to be examined)		

Fractions 4, 7, 11, and 17 have been carefully examined.

Fraction 4 contained 61% of chloroform. No satisfactory analysis was possible, but the remaining liquid contained about 34·5% S. On shaking with mercuric iodide, decanting, and evaporating in a vacuum, pale yellow crystals were obtained which dissociated very rapidly in the air and softened at 59° (Smiles, J., 1900, **77**, 164, gives m. p. 59° for $CH_3{\cdot}S{\cdot}C_2H_5,HgI_2$). The liquid (2 c.c.) reacted briskly with methyl iodide (1 c.c.) and mercuric iodide (excess). After 3 minutes, the product was washed with ether and crystallised from acetone–ether; it then formed fine yellow needles, m. p. 86° [$(CH_3)_2SI{\cdot}C_2H_5,HgI_2$ has m. p. 86°; Smiles, *loc. cit.*].

White crystals of *methyl ethyl sulphide mercurichloride* were immediately precipitated on addition of alcoholic mercuric chloride to the liquid. Several crystallisations from acetone and water gave rather unstable crystals, m. p. 101—102°.

Most of the mercurihalides here described are unstable and were purified with difficulty, immediately beginning to lose sulphide on exposure to air; the ultimate analyses, therefore, were unsatisfactory. Sintering frequently occurs during melting-point determinations and this, together with the tendency to dissociate, makes trustworthy observations difficult to obtain.

Fraction 7 contained 0·5% of chloroform. The analytical figures found (C, 56·4; H, 11·0) differ from those required for diethyl sulphide (C, 53·3; H, 11·1%), but consideration of the results obtained with fraction 11 makes it very probable that the divergence in both cases is caused by admixture of about 6% of a hydrocarbon, b. p. 100—105°.

The mercuri-iodide, prepared as described under Fraction 4, formed unstable, pale yellow crystals which did not soften below 100°. The methylsulphonium iodide mercuri-iodide formed pale yellow crystals which melted at 54° after repeated crystallisation

from acetone–ether, and the mercurichloride, unstable, white needles, which melted at 68° after repeated crystallisation from acetone by cautious addition of water. Smiles (J., 1900, **77**, 164) gives 52° as the m. p. of $(C_2H_5)_2S,HgI_2$ and 67° as that of $(C_2H_5)_2(CH_3)SI,HgI_2$, whilst for $(C_2H_5)_2S,HgCl_2$ Loir (*Annalen*, 1853, **87**, 369) records m. p. 90° and Abel (*H.*, 1895, **20**, 269) m. p. 119°. These results indicate clearly that the compound is not diethyl sulphide. No addition compounds of the above types of the methyl propyl sulphides have been described.

Fraction 11 was refractionated and the largest fraction, b. p. 64—65°/125 mm., was examined. The liquid boiled at 120—121°/760 mm. (Found: C, 56·6; H, 9·8; S, 34·0%). Di*iso*propyl sulphide (C, 61·0; H, 11·9; S, 27·1%) boils at 120·5°/763 mm. (Beckmann, *J. pr. Chem.*, 1878, **17**, 459), and tetramethylene sulphide (C, 54·5; H, 9·1; S, 36·3%) at 119° (von Braun and Trümpler, *Ber.*, 1910, **43**, 549).

The divergence from the values for tetramethylene sulphide may be ascribed to the presence of a little hydrocarbon, since derivatives were obtained in a pure state with comparative ease.

The *methiodide*, prepared in the usual way, crystallised from alcohol in fine, white needles, decomp. 185—190° (Found: I, 54·6. $C_5H_{11}IS$ requires I, 55·2%). The mercurichloride, crystallised from acetone–water, had m. p. 126° (Trochimovski, *loc. cit.*, gives m. p. 124·5—125·5°). *Tetramethylene sulphide mercuri-iodide*, prepared in the usual way, separated from acetone–water in white crystals, m. p. 58°. *Tetramethylenemethylsulphonium iodide mercuri-iodide*, prepared as previously described, formed yellow crystals, m. p. 111°.

Fraction 17 was refractionated four times; the largest fraction had b. p. 83—84°/125 mm. and 138·5°/742 mm. (Found: C, 58·5; H, 9·8; S, 31·3. Calc. for $C_5H_{10}S$, C, 58·8; H, 9·8; S, 31·4%). Low results for sulphur were obtained unless oxidation was carried out for 15 hours at 180° and then, after the pressure had been released, for 10 hours at 250°. In estimating the carbon and hydrogen, the best results were obtained by weighing the liquid in a small bubbler, which was then fixed to the end of the combustion tube, the passage of the oxygen causing steady evaporation. It seems certain that the compound is pentamethylene sulphide (compare von Braun, *loc. cit.*). The mercurichloride was prepared, and crystallised from benzene.

Pentamethylenemethylsulphonium iodide, prepared in the usual way, was converted into the sulphonium base by means of silver oxide; the solution was exactly neutralised with hydrochloric acid and gently evaporated to small bulk. The crystalline *sulphonium*

chloride obtained on cooling was precipitated from alcoholic solution with ether, washed with acetone, and dried in a vacuum over sulphuric acid. The white crystals thus obtained dissociated without melting on heating and decomposed slightly on long standing (Found: C, 46·7; H, 8·7; Cl, 22·85. $C_6H_{13}ClS$ requires C, 47·2; H, 8·6; Cl, 23·3%).

Pentamethylene sulphone was obtained in very small yield by oxidising the sulphide (2 g.) with excess of permanganate solution; it crystallised from benzene–light petroleum in white plates, m. p. 98°. Trochimovski (*loc. cit.*) gives m. p. 98·5—99°.

Pentamethylene sulphide mercuri-iodide, prepared in the usual way, was washed with ether and crystallised from acetone by cautious addition of water. The white crystals obtained, m. p. 72—74°, dissociated completely within a few hours when exposed to the air. The mercurichloride separated from benzene in white crystals, m. p. 135—136° (Trochimovski gives m. p. 137·5°). The *chloroplatinate* was obtained by adding a few drops of the sulphide to a strong aqueous solution of platinic chloride; the yellow crystals that separated after a few hours were crystallised from acetone–water. [Found: Pt, 35·4. $(C_5H_{10}S)_2PtCl_4$ requires Pt, 36·4%]. *Pentamethylenemethylsulphonium iodide mercuri-iodide*, prepared as previously described, separated from acetone–ether in yellow crystals, m. p. 78°.

The author expresses his thanks to Professor Donnan for suggesting this work and to Professor Collie and Dr. Brady for valuable advice given during its progress.

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CCCLXXIX.—*Condensations of the Sodium Derivatives of Trimethylene Glycol and Glycerol.*

By ARTHUR FAIRBOURNE and GRAHAM EDWARD FOSTER.

IN extension of the work on the condensation of 1-chloro-2 : 4-dinitrobenzene with glycerol (J., 1921, **119**, 1035) and ethylene glycol (*ibid.*, p. 2077), the similar condensation in the case of trimethylene glycol has now been investigated.

A solution of the sodium derivative is readily obtained by dissolving sodium in excess of trimethylene glycol and may be used for effecting the condensation. In spite of the large excess of glycol present, and although monosodium glyceroxide gives rise to only

one product in the corresponding reaction (*loc. cit.*, p. 1037), both mono- and bis-dinitrophenyl ethers of trimethylene glycol are produced, even when the chlorodinitrobenzene is added slowly.

$$\begin{array}{l}\mathrm{CH_2{\cdot}OH}\\ \mathrm{CH_2}\\ \mathrm{CH_2{\cdot}OH}\end{array} \longrightarrow \text{(I.)}\ \begin{array}{l}\mathrm{CH_2{\cdot}OH}\\ \mathrm{CH_2}\\ \mathrm{CH_2{\cdot}O{\cdot}C_6H_3(NO_2)_2}\end{array} + \begin{array}{l}\mathrm{CH_2{\cdot}O{\cdot}C_6H_3(NO_2)_2}\\ \mathrm{CH_2}\\ \mathrm{CH_2{\cdot}O{\cdot}C_6H_3(NO_2)_2}\end{array} \text{(II.)}$$

The relative yields of these ethers vary with the concentration of the sodium derivative and therefore may be regarded as dependent on the tendency to set up the equilibrium

$$\begin{array}{l}\mathrm{CH_2{\cdot}O{\cdot}C_6H_3(NO_2)_2}\\ \mathrm{CH_2}\\ \mathrm{CH_2{\cdot}OH}\end{array} + \begin{array}{l}\mathrm{CH_2{\cdot}OH}\\ \mathrm{CH_2}\\ \mathrm{CH_2{\cdot}ONa}\end{array} \rightleftharpoons \begin{array}{l}\mathrm{CH_2{\cdot}O{\cdot}C_6H_3(NO_2)_2}\\ \mathrm{CH_2}\\ \mathrm{CH_2{\cdot}ONa}\end{array} + \begin{array}{l}\mathrm{CH_2{\cdot}OH}\\ \mathrm{CH_2}\\ \mathrm{CH_2{\cdot}OH}\end{array}$$

it being assumed, as in the two previous papers, that the primary condensation involves merely the replacement of the sodium by the substituent group:

$$\mathrm{R{\cdot}O{\cdot}Na + Cl{\cdot}C_6H_3(NO_2)_2 \longrightarrow R{\cdot}O{\cdot}C_6H_3(NO_2)_2.}$$

On this assumption depend the arguments previously put forward in support of the structure of glycerides (*loc. cit.*, p. 1035). Doubt was cast on its validity, however, by the accidental preparation of the bisdinitrophenyl ether above mentioned and by the further discovery that *tri*-substituted derivatives of glycerol can be obtained by treating monosodium glyceroxide, suspended in an inert solvent, with *one* equivalent of certain acid chlorides, a reaction not contemplated in the previous papers.

$$\begin{array}{l}\mathrm{CH_2{\cdot}OH}\\ \mathrm{3CH{\cdot}OH}\\ \mathrm{CH_2{\cdot}ONa}\end{array} + \mathrm{3Ph{\cdot}SO_2Cl} \longrightarrow \begin{array}{l}\mathrm{CH_2{\cdot}SO_3Ph}\\ \mathrm{CH{\cdot}SO_3Ph}\\ \mathrm{CH_2{\cdot}SO_3Ph}\end{array} + \begin{array}{l}\mathrm{CH_2{\cdot}OH}\\ \mathrm{2CH{\cdot}OH}\\ \mathrm{CH_2{\cdot}OH}\end{array}$$

Moreover, such trisubstituted products were obtained from disodium glyceroxide under identical conditions:

$$\mathrm{3C_3H_6O_3Na_2 + 6Ph{\cdot}COCl} \longrightarrow \begin{array}{l}\mathrm{CH_2{\cdot}CO_2Ph}\\ \mathrm{2CH{\cdot}CO_2Ph}\\ \mathrm{CH_2{\cdot}CO_2Ph}\end{array} + \begin{array}{l}\mathrm{CH_2{\cdot}OH}\\ \mathrm{CH{\cdot}OH}\\ \mathrm{CH_2{\cdot}OH}\end{array}$$

It was realised that the formation of these substances might be due to direct interaction of labile chlorine atoms and hydroxyl groups,

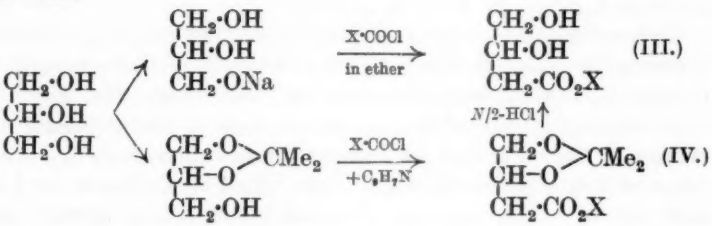
$$\begin{array}{l}\mathrm{CH_2{\cdot}ONa}\\ \mathrm{CH_2}\\ \mathrm{CH_2{\cdot}OH}\end{array} + \mathrm{2Cl{\cdot}C_6H_3(NO_2)_2} \longrightarrow \begin{array}{l}\mathrm{CH_2{\cdot}O{\cdot}C_6H_3(NO_2)_2}\\ \mathrm{CH_2}\\ \mathrm{CH_2{\cdot}O{\cdot}C_6H_3(NO_2)_2}\end{array},$$

the excess of the sodium derivative merely serving to destroy the hydrogen chloride thus formed. Glycerol, ethylene glycol, and

trimethylene glycol were therefore heated separately with 1-chloro-2 : 4-dinitrobenzene in presence of calcium carbonate, and trimethylene glycol mono-2 : 4-dinitrophenyl ether was treated similarly in presence of sufficient inert solvent to dissolve all organic matter, but in no case was there a trace of ionisable halogen in the product. It appears clear, therefore, that no condensation between halogen atoms and hydroxyl groups occurs during the reactions with chlorodinitrobenzene, and that the chlorine removes the sodium in the way previously assumed.

The production from sodium glyceroxide of the tri-ester mentioned above might be explicable in the light of Fischer's observation (*Ber.*, 1920, **53**, 1621, 1634) that mono-esters of polyhydric alcohols in ethereal solution in presence of a catalyst such as potassium carbonate or sodium ethoxide are moderately rapidly transformed into di-esters and free alcohols. A similar explanation is untenable, however, in the case of trimethylene glycol bisdinitrophenyl ether, for when the mono-ether was treated with a solution of sodium in trimethylene glycol under the conditions existing during the condensation with chlorodinitrobenzene no bis-ether was found in the product, the very different solubilities of the mono- and bis-ethers in acetic acid rendering the absence of the latter easily provable.

The α-structure of monosodium glyceroxide (*loc. cit.*, p. 1036) has been confirmed by the following series of reactions using *iso*propylidene glycerol (Irvine, Soutar, and Macdonald, J., 1915, **107**, 337; Fischer, *Ber.*, 1920, **53**, 1589), X denoting p-$C_6H_4{\cdot}NO_2$ or 3 : 5-$C_6H_3(NO_2)_2$:



EXPERIMENTAL.

Trimethylene Glycol Mono-2 : 4-dinitrophenyl Ether (I).—Sodium (1·14 g.) was dissolved, in small portions to prevent charring, in 40 c.c. of trimethylene glycol, and the solution was stirred and heated at 100° while a suspension of 10·2 g. of 1-chloro-2 : 4-dinitrobenzene in 30 c.c. of the glycol was gradually added. Heating and stirring were continued until the chlorodinitrobenzene dissolved (½ hour). The product was poured into 1000 c.c. of 20% acetic acid an oil

being precipitated. The whole was boiled for 30 minutes; most of the oil had then redissolved and the remainder had crystallised (A). The solution was filtered, and cooled to 0° after 24 hours. The colourless needles deposited were dried in a vacuum over sulphuric acid and recrystallised from benzene–ligroin (b. p. 40—60°). The *ether* thus obtained (yield 6 g.), m. p. 52°, was soluble in ether, benzene, alcohol, acetone, or acetic acid, and sparingly soluble in water or ligroin (Found: N, 11·5. $C_9H_{10}O_6N_2$ requires N, 11·55%).

The *acetyl* derivative prepared by heating the ether for a few minutes with 2 vols. of acetyl chloride and acetic anhydride (equal parts) and boiling the product with much water, separated from the filtered solution in long, colourless needles, m. p. 85°, the yield being nearly quantitative (Found: C, 46·1; H, 4·45; N, 9·9. $C_{11}H_{12}O_7N_2$ requires C, 46·4; H, 4·25; N, 9·9%).

The *benzoyl* derivative was prepared by shaking a warm mixture of the ether and benzoyl chloride with successive small quantities of 20% sodium hydroxide solution, added in sufficient amount to prevent the orange colour from being discharged; water was then added. The *benzoyl* derivative, obtained as a semi-solid mass on cooling the mixture, separated from alcohol in colourless crystals, m. p. 95°, soluble in most of the common organic solvents (Found: N, 8·2. $C_{16}H_{14}O_7N_2$ requires N, 8·11%).

Trimethylene Glycol Bis-2 : 4-dinitrophenyl Ether (II).—The substance (A) mentioned above was sparingly soluble in alcohol, ether, or acetone, but by recrystallisation from boiling glacial acetic acid the bis-*ether* was obtained in colourless needles (yield 0·5 g.), m. p. 180° (Found: C, 44·0; H, 3·2; N, 13·4. $C_{15}H_{12}O_{10}N_4$ requires C, 44·1; H, 3·0; N, 13·6%).

Glyceryl Tri-p-toluenesulphonate, $C_3H_5(O{\cdot}SO_2{\cdot}C_7H_7)_3$.—Disodium glyceroxide was prepared by the method of Löbish and Loos (*Monatsh.*, 1881, **2**, 842) (Found: Na, 33·0. Calc., Na, 33·8%).

A mixture of equimolecular proportions of either mono- or di-sodium glyceroxide and *p*-toluenesulphonyl chloride in dry ether or benzene was kept for 24 hours, then boiled under reflux for ¼ hour, and filtered. The *glyceride* obtained on distilling off the solvent slowly solidified, and crystallised from alcohol in colourless needles, m. p. 103° (Found: C, 51·6, 51·8; H, 4·8, 4·8; S, 17·4; *M*, cryoscopic in benzene, 564. $C_{24}H_{26}O_9S_3$ requires C, 52·0; H, 4·7; S, 17·3%; *M*, 554).

Glyceryl tribenzenesulphonate, obtained in a similar way from benzenesulphonyl chloride, crystallised from alcohol in needles, m. p. 80° (Found: C, 49·0; H, 3·9. $C_{21}H_{20}O_9S_3$ requires C, 49·2; H, 3·9%).

Action of Benzoyl Chloride upon Sodium Glyceroxides.—The

products obtained by the action of an ethereal solution of benzoyl chloride on mono- and di-sodium glyceroxides were not identical.

Monosodium glyceroxide yielded α-monobenzoyl glycerol (compare *loc. cit.*, p. 1340).

Disodium glyceroxide yielded tribenzoyl glycerol, which, even after repeated crystallisation from ligroin, melted at 71—72° (Found: C, 71·25; H, 4·95. Calc., C, 71·3; H, 4·95%). The m. p. is given by Skraup (*Monatsh.*, 1889, **10**, 393) as 75—76·5°, by Balbiano (*Ber.*, 1903, **36**, 1574) as 71—72°, and by Krafft (*ibid.*, p. 4341) as 76°. A comparison of these references and others showed that the substance melted at 76° or 72° according as it had been crystallised from alcohol or ligroin. The above product was therefore crystallised from alcohol. It then melted at 76°. Subsequent recrystallisation from ligroin (b. p. 40—60°), or slow solidification of the fused material, reduced it to 72° again.

Action of p-*Nitrobenzoyl Chloride upon Monosodium Glyceroxide.*—Monosodium glyceroxide was treated with an equivalent quantity of *p*-nitrobenzoyl chloride in ethereal solution, and the reaction carried out in the usual manner. The product obtained by filtration and evaporation of the solvent was an oil which solidified on cooling and crystallised from chloroform in needles, m. p. 107°. A mixture of this with a specimen of α-mono-*p*-nitrobenzoyl glycerol (m. p. 107°) prepared by Fischer's method (*Ber.*, 1920, **53**, 1596) also melted at 107°. In the preparation of *iso*propylidene glycerol as an intermediate product in the second method, the resulting liquid boiled at 78—79°/10 mm.

iso*Propylidene Glycerol* 3 : 5-*Dinitrobenzoate* (IV).—A mixture of 11·6 g. of 3 : 5-dinitrobenzoyl chloride and 8·2 g. of dry quinoline was dissolved in 15·6 c.c. of chloroform, 6·7 g. of *iso*propylidene glycerol were slowly added with cooling, and the whole was kept for 2 days. The product was shaken successively with water, dilute sulphuric acid, sodium bicarbonate solution, and water, then dried over ignited sodium sulphate, and the solvent removed. The residual oil solidified on cooling, and crystallised from ligroin (b. p. 40—60°) –benzene in colourless needles (yield 80%), m. p. 85°, soluble in benzene, ether, or chloroform, and nearly insoluble in ligroin (Found: N, 8·6. $C_{13}H_{14}O_8N_2$ requires N, 8·6%).

Glycerol α-*Mono*-3 : 5-*dinitrobenzoate* (III).—(a) A mixture of equivalent quantities of monosodium glyceroxide and 3 : 5-dinitrobenzoyl chloride in ether was kept for 2 days and then heated under reflux. The suspended matter, which had little or no alkaline reaction, was filtered off, and the solvent evaporated. The residual oil, which solidified, crystallised from chloroform in colourless needles, m. p. 118°, soluble in alcohol, ether, or benzene; it also

crystallised easily from water (Found: N, 9·75. $C_{10}H_{10}O_8N_2$ requires N, 9·79%).

(b) A mixture of 5 g. of *iso*propylidene glycerol 3 : 5-dinitrobenzoate and 100 c.c. of *N*/2-hydrochloric acid was stirred and heated at 70—80° for 1 hour. The clear liquid was decanted, and deposited glycerol α-dinitrobenzoate on cooling. This, after being dried in a vacuum over sulphuric acid and crystallised from chloroform (yield 70%), melted at 118°, alone or mixed with a specimen prepared by method (a).

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CCCLXXX.—*The Formation and Growth of Silver Nuclei in the Decomposition of Silver Oxalate.*

By JAMES YOUNGER MACDONALD and CYRIL NORMAN HINSHELWOOD.

THIS paper contains first a description of a sensitive method for making direct measurements of the instantaneous rate of reaction in a chemical change where gas is evolved, and secondly an account of its application in the investigation of certain interesting phenomena relating to the thermal decomposition of silver oxalate.

The decomposition of solid substances frequently offers the appearance of being autocatalytic, the rate of change increasing as the reaction progresses. This is in many instances due simply to an increase in the surface of the solid during the course of the transformation (*Phil. Mag.*, 1920, **40**, 569), but it can also be due to the circumstance that the reaction is facilitated by the presence of nuclei of one of the products. To whichever cause the acceleration is due, the relation between the velocity of change and the amount of reaction which has already taken place is a very complicated one. The determination of this relation from measurements of the total change, x, which has taken place at any time, t, depends upon the drawing of tangents to curves of x and t, a procedure involving a large proportional error. The following method was therefore adopted for obtaining direct readings of the actual velocity at different times during the reaction.

The solid is allowed to decompose in a small bulb kept at constant temperature in a vapour bath. The bulb is connected with a

McLeod gauge and the gaseous products of the reaction are removed by a continuously running Gaede pump. The experiments must be made at temperatures where the rate of evolution of gas is not too great, so that the pump is able to maintain a fairly high vacuum in the apparatus. At intervals measurements of the rate of reaction are made by turning off the tap leading to the pump and raising the mercury in the McLeod gauge for a pressure reading. At the moment when the mercury cuts off the bulb of the gauge from communication with the decomposition vessel a stop-watch is started. The pressure reading is completed and the mercury lowered, communication with the decomposition vessel being once more established. At the end of a suitable time a second reading of the McLeod gauge is made, the watch being stopped at the moment when the mercury once more cuts off the gauge from the rest of the apparatus. In the actual experiments pressure increases of the order of 0·1 or 0·01 mm. were measured in periods of time varying from 45 seconds to 15 minutes in reactions lasting several hours or days. The readings, therefore, can be regarded as instantaneous. By the use of gauges of various degrees of sensitiveness in different experiments it is possible either to follow the reaction over its whole course or to make a more detailed study of the initial stages.

No investigation has previously been made of the mechanism of the decomposition of silver oxalate. It is usually assumed that the change takes place in accordance with the simple equation $C_2O_4Ag_2 = 2Ag + 2CO_2$. This was confirmed by an analysis of the residue, which was more than 99·8% silver, and of the gas, which was pure carbon dioxide containing no trace of carbon monoxide. If the reaction involved the intermediate formation of carbonate or oxide, carbon monoxide would necessarily appear in the gaseous products.

Various specimens of silver oxalate behaved very differently, falling roughly into two classes. One class decomposed with the most marked acceleration, the maximum velocity being about 200 times greater than the initial velocity. The other class showed very much less acceleration, and the velocity, instead of passing through a sharp maximum, remained steady over a large part of the whole course. Specimens of this second class were on the whole about ten times as stable as those of the first class. The difference was traced to one factor in the method of preparation. All the specimens were prepared by precipitation of silver nitrate with sodium oxalate. Those precipitated under such conditions that the sodium oxalate was in excess throughout belonged to the unstable accelerating type, whilst those precipitated with silver nitrate always in excess belonged to the stable, feebly accelerating type.

The method of preparation was carefully standardised. The precipitant which was not to be in excess was run slowly as a fine continuous stream in the course of about ½ hour into a solution of the other salt, which was vigorously agitated by a mechanical stirrer. All the solutions were very dilute—an obvious precaution in view of Richards' well-known investigation of the occlusion difficulties of Stas—and the precipitation was carried out in blackened vessels at the ordinary temperature. The silver oxalate was repeatedly washed by decantation, and dried in a vacuum desiccator kept in a dark cupboard. As far as we are able to judge, all factors were exactly the same in the preparation of the two types of silver oxalate except that one or other precipitant was in excess.

The autocatalytic acceleration is not due to carbon dioxide, since it takes place in a vacuum. It is not due simply to increase in surface, as with potassium permanganate and some other solids (*loc. cit.*), since it cannot be eliminated by preliminary grinding. It must be due, therefore, to nuclei of solid silver formed in the decomposition. Since the initial velocity is very small compared with that finally attained, the whole course of the reaction is evidently governed by the formation and growth of these nuclei. The decomposition of solids is essentially a surface phenomenon. Moreover, the devitrification of glass, which depends upon the formation of crystal nuclei, is known to start from the surface, since the washing of the surface with dilute hydrofluoric acid removes the tendency to further devitrification on heating. It is very probable that in a similar way the silver nuclei are formed at the surface of the oxalate crystals. The formation of nuclei and their subsequent growth are independent phenomena both of which are extremely sensitive to the presence of foreign substances (compare Zsigmondy, "Kolloidchemie," 1922, p. 144). When silver oxalate is precipitated with excess of silver nitrate and sodium oxalate, respectively, there will probably be different ions adsorbed. The different behaviour of the oxalate prepared by these two methods is to be attributed to the effect of the adsorbed ions on the chance of formation of silver nuclei in the solid and on their subsequent growth.

As the silver oxalate was always very thoroughly washed during preparation, only the definitely adsorbed ions need be taken into account.

The decomposition bulb was protected from light by a covering of tinfoil.

About fifty experiments were carried out with twelve specimens of oxalate. Some of the results are in the following tables and curves; t is the time in minutes, and v the velocity of reaction in arbitrary units.

Temperature 131·8°.

(*a*) Silver oxalate precipitated with excess of sodium oxalate.

t.	*v.*	*t.*	*v.*
5	5·3	39·5	756
12	60	43	628
18	147·5	49	434
21	216	53	340
25	384	60	192
28·5	725	75	154
30·5	958	96	46
32·5	850	140	28·5
35·5	888	263	13·3

This specimen was precipitated with a very large excess of oxalate, and is one of the most unstable.

(*b*) Silver oxalate precipitated with excess of silver nitrate.

t.	*v.*	*t.*	*v.*
3·5	7	240	48
10	13	270	50
33	32	305	48
43	28	335	31
47	33	360	24
60	31	420	18
105	50	540	13
150	43	600	6·3
180	43		

The rise and fall in velocity is quite real, and presumably connected with the fact that the oxalate grains are not quite uniform.

Using a more sensitive gauge it is possible to see in more detail the initial variations in rate. The following results were obtained with a rather more stable specimen of oxalate. Up to 100 minutes, the decomposition amounts to about 1% only. Temperature 131·6°.

t.	*v.*	*t.*	*v.*	*t.*	*v.*	*t.*	*v.*
5	3·4	32·5	45·8	77·5	224	135	477
12·5	3·9	37·5	62·8	86·5	255	149	516
17·5	5·8	47·5	107·2	97·5	310	165	549
22·5	15·6	58·5	152	110·5	374	198·5	580
27·5	26·8	67·5	183	121	407	204·5	618

In this experiment, the maximum rate of nearly 3000 was reached in about 6 hours.

It is worth while to give in full the results of one more experiment, made at 110° with a specimen of the accelerating type. Attention may be directed to the long period of steady velocity following the sharp fall from the maximum.

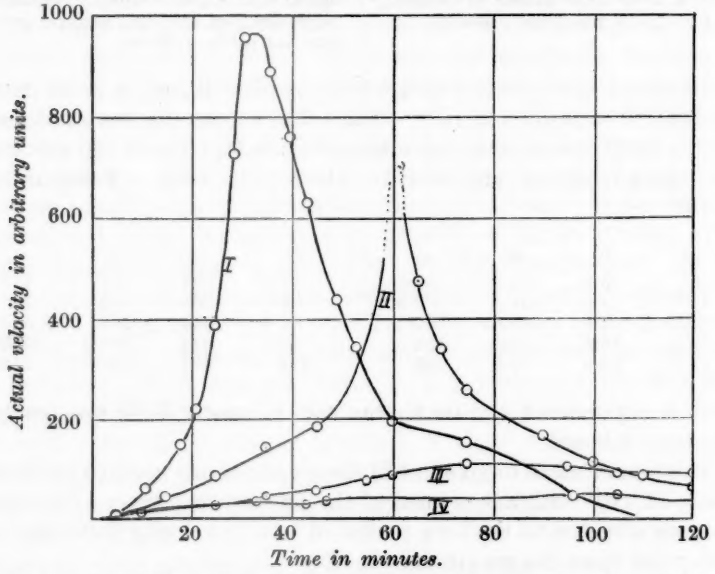
t.	*v.*	*t.*	*v.*	*t.*	*v.*
5	1·09	759	182	2,405	83·2
15	1·22	832	214·5	2,575	83·5
25	1·28	881	224·5	2,813	78·7
40	1·79	936	251	3,127	72·9
60	2·70	1,126	298	3,858	51·4
85	4·72	1,197	276	4,303	45·9
135	12·0	1,331	228	5,180	33·7
170	18·6	1,400	189·5	6,012	25·7
245	35·7	1,607	115	6,708	19·3
313	50·0	1,737	98·0	8,873	16·7
438	69·4	2,293	78·0	9,617	14·1
533	90·8	2,310	82·9	13,920	8·7
				19,700	5·6

The relation between the velocity and the amount decomposed is not by any means simple. G. N. Lewis, investigating the some-

what similar decomposition of silver oxide (*Z. physikal. Chem.*, 1905, **52**, 310), thought that the results could be expressed by the simple equation for homogeneous autocatalysis $dx/dt = kx(a - x)$. It is difficult to see how the complex process of nucleus formation and growth can be so represented. The applicability of the equation to the silver oxalate decomposition can be tested in two ways. (*a*) dx/dt is plotted against t and, by square counting, a curve of x and t is constructed. It is then readily seen by plotting $\log [dx/dt/(a - x)]$ against $\log x$ whether the rate per unit amount

FIG. 1.

Influence of the method of precipitation on the decomposition of silver oxalate.



Curves I and II: silver oxalate precipitated in presence of excess of sodium oxalate. Curves III and IV: excess of silver nitrate.

of oxalate is a linear function of x. It is not. The rate depends upon a power of x which not only varies but is always less than unity. (*b*) For the very early stages of the reaction, as measured with a more sensitive gauge, the equation reduces to $dx/dt = kx$, but to account for the fact that the reaction starts at all this has in any case to be written $dx/dt = k\ (x + x_0)$, where x_0 is a small constant quantity which determines the actual initial rate. From this it follows that $\log dx/dt = kt +$ constant. This gives a convenient means of plotting the results without resorting to the laborious process of square counting. The following table contains a set of typical results, the figures referring to the initial stages of

one of the experiments already quoted (second table). $dx/dt = v$. When $t = 5$, $\log v = 0{\cdot}53$.

$t - 5$.	$\log v - 0{\cdot}53$.	$\frac{\log v - 0{\cdot}53}{t - 5}$.	$t - 5$.	$\log v - 0{\cdot}53$.	$\frac{\log v - 0{\cdot}53}{t - 5}$.
12·5	0·23	0·0184	53·5	1·652	0·0309
17·5	0·663	0·0379	62·5	1·713	0·0274
22·5	0·898	0·0399	72·5	1·820	0·0251
27·5	1·131	0·0412	81·5	1·877	0·0230
32·5	1·268	0·0390	92·5	1·961	0·0212
42·5	1·500	0·0353	105·5	2·043	0·0194

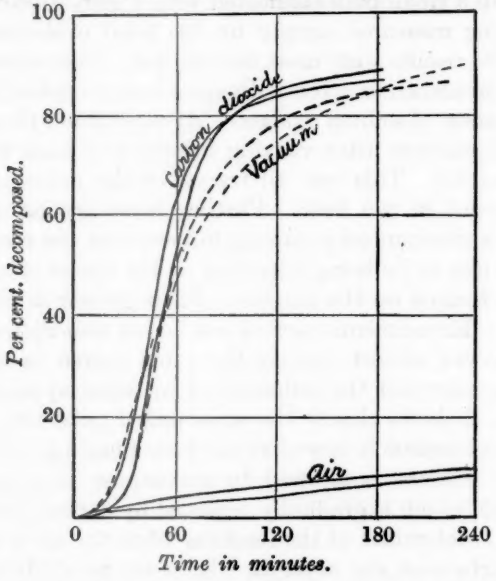
Influence of Adsorbed Gases on the Silver Nuclei.—Some experiments were also made in which the silver oxalate was allowed to decompose in a small bulb connected with a gas burette, the rate of reaction being measured simply by the total evolution of carbon dioxide. The results were most unexpected. Sometimes there was no trace of acceleration, even with specimens prepared by precipitation with excess of sodium oxalate. At other times the acceleration made its appearance after varying intervals of time in an uncontrollable manner. This was all traced to the influence of the air initially present in the bulb. Further investigation showed that oxygen has a pronounced poisoning influence on the reaction. This is evidently due to its being adsorbed on the nuclei of silver as soon as they are formed on the surface. Their growth is thus hindered or stopped. Experiments carried out in an atmosphere of carbon dioxide followed almost exactly the same course as those carried out in a vacuum and the influence of nitrogen appears to be but slight. Fig. 2 shows clearly the pronounced poisoning influence of air. The explanation is now obvious of the puzzling results obtained when silver oxalate is allowed to decompose in a bulb initially filled with air which is gradually replaced by carbon dioxide; there is a sudden acceleration of the reaction when the air is all displaced from the surface of the crystals. In order to study the reaction under conditions where the poisoning effect of air was constant, experiments were made in a stream of air, the rate of reaction being measured periodically by cutting off the stream and allowing the pressure to rise. The stream was sufficiently slow for there to be no appreciable cooling effect, as the air passed through a considerable length of heated tubing before actually coming into contact with the silver oxalate. In a continuous stream of air, or even in the presence of still air the reaction is spread out over a time about ten times as long as in a vacuum or in presence of carbon dioxide. The poisoning effect is relatively more marked with the unstable accelerating specimens precipitated with excess of sodium oxalate than with those precipitated in presence of an excess of silver

nitrate, since in the latter the acceleration is already to some extent inhibited.

The changes in colour which accompany the decomposition are interesting, the white oxalate passing through pale to deep brown and then becoming black. When the reaction is nearly complete some sort of recrystallisation of the silver seems to occur and the whole mass becomes almost white. Addition of the final product does not cause an increase in the rate of reaction. Evidently coarser particles of silver are not effective in catalysing the change in the same way as the minute nuclei formed in the space lattice of

FIG. 2.

Influence of air on the decomposition of silver oxalate.



the oxalate crystals themselves. Experiments were made on the influence of previous grinding. This produced some increase in the rate of reaction, but did not eliminate the autocatalysis as with potassium permanganate and some other solids.

The influence of temperature was investigated with a few of the specimens. It is normal, and more or less uniform throughout all stages of the decomposition. Over the range 100° to 150° the rate increases approximately 2·7 times for 10°.

Summary.

The thermal decomposition of silver oxalate takes place in accordance with the simple equation $(CO{\cdot}OAg)_2 = 2Ag + 2CO_2$.

Its rate is governed entirely by the formation and growth of nuclei of silver in the space lattice of the oxalate crystals.

These processes are sensitive to the presence of adsorbed ions, since silver oxalate precipitated in presence of excess of sodium oxalate behaves quite differently from that precipitated in presence of excess of silver nitrate. This is in some respects analogous to the influence of adsorbed ions on the photo-sensitivity of silver bromide described by Fajans and Frankenburger (*Z. Elektrochem.*, 1922, **28**, 499).

In a vacuum and in an atmosphere of carbon dioxide the rate of reaction is the same, but the presence of oxygen has a very pronounced poisoning effect on the silver nuclei. This is an example of catalytic poisoning of a new kind. The influence of adsorbed ions and of oxygen seems to show that the nuclei must be first formed at the surface of the oxalate crystals, rather than at any point in the interior.

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CCCLXXXI.—*The Influence of Different Nuclei on the Absorption Spectra of Substances.*

By JOHN EDWARD PURVIS.

IN previous papers (J., 1914, **105**, 590, 1372) the author described the absorption spectra of substances containing several benzene nuclei, and it was shown that the phenomena were very different in substances containing two, three, and four benzene residues even when the nuclei with which they were combined had no specific absorption.

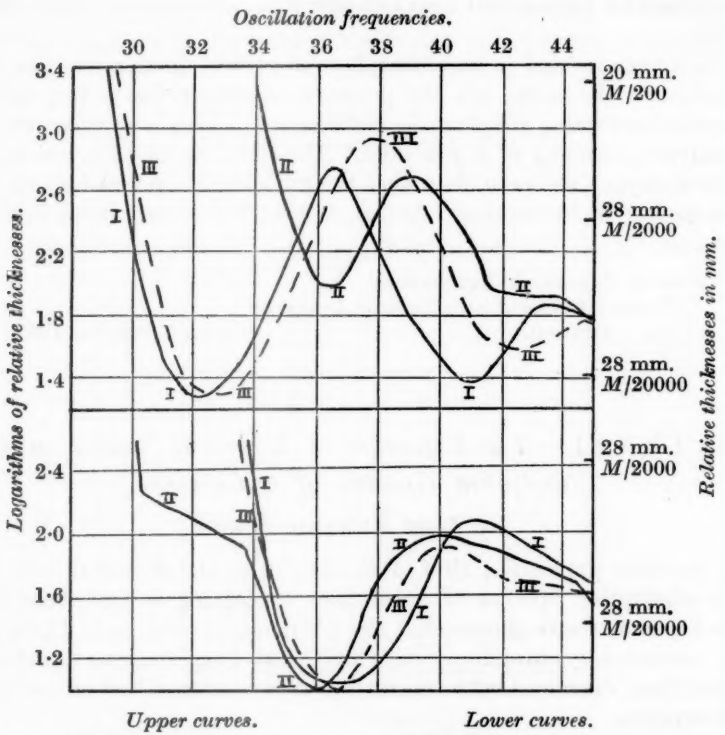
The aim of this communication is to describe the absorption spectra in the ultra-violet region (1) of substances in which each nucleus shows specific absorption when uncombined, and (2) of substances in which only one of the nuclei shows specific absorption.

Alcoholic solutions of the following substances were examined: Salicylic acid, phenyl salicylate, *o*-acetoxybenzoic acid, benzyl salicylate, thymol salicylate, camphor, camphor salicylate, theobromine, theobromine salicylate, theobromine *o*-acetoxybenzoate, caffeine, caffeine salicylate, caffeine benzoate, caffeine citrate, caffeine hydrochloride, phenazone, phenazone salicylate, quinine, quinine salicylate, and quinine *o*-acetoxybenzoate. Most of the substances were examined in the first instance in *M*/200-solution,

but theobromine and caffeine and their salicylates were soluble only in about $M/2{,}000$-strength. A condensed cadmium spark was the source of radiant energy.

Salicylic acid. Hartley's observation (J., 1888, **53**, 641) that this substance has two bands in the ultra-violet region has been confirmed.

FIG. 1.



Upper curves.

I *Phenyl salicylate.*
II o-*Acetoxybenzoic acid.*
III *Camphor salicylate.*

Lower curves.

I *Theobromine.*
II *Theobromine salicylate.*
III *Theobromine* o-*acetoxybenzoate.*

Phenyl salicylate. This has two bands like those of the acid. On comparing photographs of the two substances it was clear that there was a shift towards the red end and the less refrangible band of the salt was not so strong as that of the acid; and also the more refrangible band was better marked. Fig. 1, I (upper series) gives the curve for the salt.

o-*Acetoxybenzoic acid.* The replacement of the hydrogen in the hydroxyl group by acetyl has produced a striking change in the absorption (Fig. 1, II, upper series). The less refrangible band at

1/λ3650 (λ2740) is much weaker and is shifted towards the more refrangible regions. When the spectrum is compared with that of salicylic acid or phenyl salicylate, the more refrangible band is represented by an extension of the rays from 1/λ4150 (λ2408) to 1/λ4350 (λ2298). The general appearance of the absorption is not unlike that of benzoic acid and this is usually assigned to the benzene nucleus.

Thymol salicylate. Benzyl salicylate. The bands of these two substances were similar to those of salicylic acid and phenyl salicylate, and differed chiefly in position, corresponding to differences in their respective molecular weights. The three benzene bands of the benzyl nucleus do not appear as they do in such substances as dibenzyl carbamate and benzyl chloride (Purvis, J., 1914, **105**, 1372; 1915, **107**, 496). The curves have not been reproduced.

Camphor salicylate. The curve (Fig. 1, III, upper series) shows that the two bands of the acid have not been very much affected. The differences are that the less refrangible band is not so strong as that of salicylic acid or of phenyl salicylate, and the more refrangible band is weaker. Camphor has a weak band at 1/λ3480 (λ2870) as described by Baly, Marsden, and Stewart (J., 1906, **89**, 979) and confirmed by Hartley (J., 1908, **93**, 961) and by the author (J., 1915, **107**, 643).

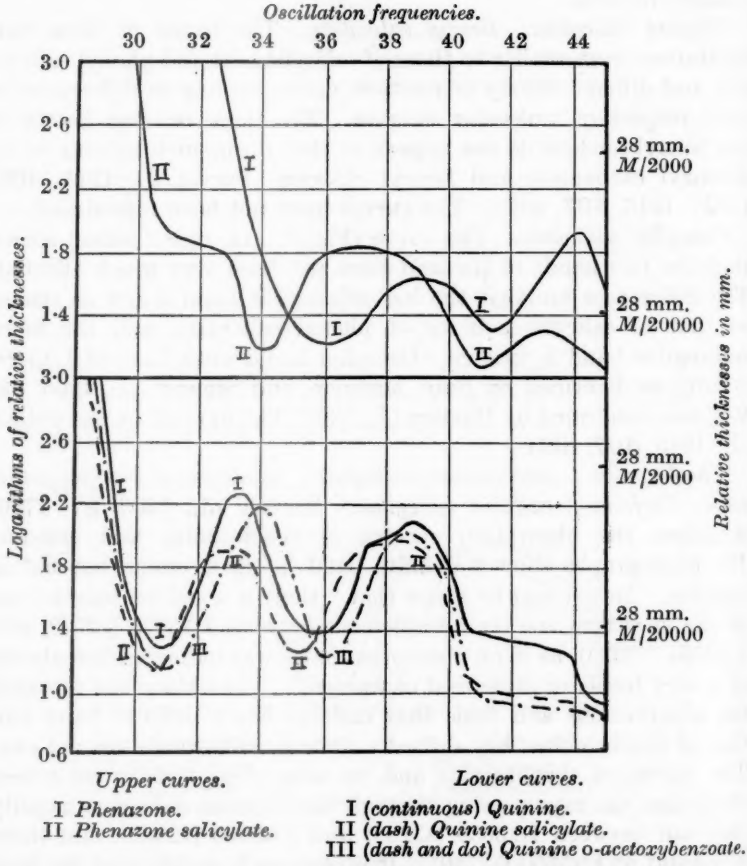
Theobromine; theobromine salicylate; theobromine o-*acetoxybenzoate. Caffeine; caffeine salicylate.* Hartley (J., 1905, **87**, 1796) describes the absorption spectra of theobromine and caffeine. His photographs show a definite band in theobromine but not in caffeine. In the text he states that "there is a sudden lengthening of the spectrum and its enfeeblement between 1/λ3675 (λ2720) and 1/λ3794 (λ2635), as if an absorption band was indicated hereabouts of a very feeble or ill-defined character." The author has repeated the observations and finds that caffeine has a definite band like that of theobromine, but shifted a little more towards the red end. The curves of theobromine and its salts (Fig. 1, I, lower series) show that the rays passing through theobromine salicylate rapidly step out between 1/λ3030 (λ3298) and 1/λ3350 (λ2980), and there is a band at 1/λ3650 (λ2740). It is obvious from this that the acid nucleus exerts some influence on the absorption. The curve of theobromine *o*-acetoxybenzoate shows considerable differences. It is not unlike that of theobromine itself but narrower, and the ultimate effect is comparable with that of salicylic acid and *o*-acetoxybenzoic acid described above.

Solutions of caffeine and caffeine salicylate show similar phenomena to theobromine and theobromine salicylate.

Caffeine benzoate: caffeine citrate: caffeine hydrochloride. Solu-

tions of these salts give results like those of the base itself, except in regard to the positions of the bands, which vary according to the molecular weights. The author (J., 1915, **107**, 966) showed that benzoic acid has a weak band at 1/λ3600 (λ2770), and also that there was a rapid step-out of the rays from about λ2320 into the

FIG. 2.



Schumann region. Hartley and Hedley earlier (J., 1909, **91**, 314) had indicated the presence of the weak band only. It is clear, therefore, that the acid nucleus has not affected the general form of the caffeine absorption. Neither citric acid nor hydrochloric acid gives specific absorption in these ultra-violet regions. The curves have not been reproduced.

Phenazone; phenazone salicylate. The curve shows (Fig. 2, upper curves) that phenazone has two wide bands at 1/λ3600 (λ2776)

and 1/λ4150 (λ2409). The salt shows a rapid extension of the rays between 1/λ3050 (λ3270) and 1/λ3260 (λ3066), and two weak bands at 1/λ3400 (λ2940) and 1/λ4100 (λ2438). As in theobromine and caffeine, the rapid extension of the rays may mean the remnant of the less refrangible band of salicylic acid.

Quinine, quinine salicylate, quinine o-*acetoxybenzoate.* Hartley (*Phil. Trans.*, 1885, **176**, 471) first described two bands in solutions of quinine at about 1/λ3100 (λ3225) and 1/λ3600 (λ2770). Dobbie, Lauder, and Fox (J., 1911, **99**, 1254; 1912, **101**, 77) described a third weak band at 1/λ3740 (λ2670). The author has repeated these experiments and finds only a very weak indication of this third band. The curves (Fig. 2, lower curves) show that the original quinine bands have suffered some changes in strength and position in the salicylate. Both the bands of the salicylate are weaker than those of the base. In the case of the *o*-acetoxybenzoate there is a return to phenomena not unlike those of the base itself, and there is a shift back nearer to the latter. These changes are comparable (although the differences are not so great) with those of salicylic acid and *o*-acetoxybenzoic acid and of theobromine and its salts described above. The rapid extension of the rays from 1/λ4100 is noticeable in all three substances.

Results.—The chief results of these observations are: (1) the bands of phenyl, benzyl, thymol, and camphor salicylates are comparable with those of salicylic acid: the differences from the latter, and from one another, being chiefly in position and strength; (2) the basic nucleus is the chief agent in the specific absorption of the benzoate, citrate and hydrochloride of caffeine; (3) in the salicylates of theobromine, caffeine, phenazone and quinine, the acid nucleus modifies that of the basic nucleus to a larger extent, but least in the quinine compound: (4) in *o*-acetoxybenzoic acid, and in the *o*-acetoxybenzoates of theobromine and quinine the replacement of the hydrogen of the hydroxyl group by the acetyl group exerts a very great influence on the final absorption.

It is clear, therefore, that the specific and the general absorption of these substances depend upon three factors; (*a*) the nature of the base, (*b*) the nature of the acid, and (*c*) the presence of hydrogen in the hydroxyl group. Now benzoic acid has a very weak band at 1/λ3600 (λ2777) and phenol a very strong one at 1/λ3670 (λ2720). The carboxyl group in the one and the hydroxyl group in the other destroy the well-known bands of benzene: and the hydroxyl group replaces these by a much stronger one than is produced by the carboxyl group. It appears from these experiments that the replacement of the hydrogen atom of the hydroxyl group by another radical, not itself possessing any specific absorption, decreases the

absorption capacity of the other parts of the molecule: or, to put it another way, the vibration of this hydrogen atom is a very powerful factor in the absorption.

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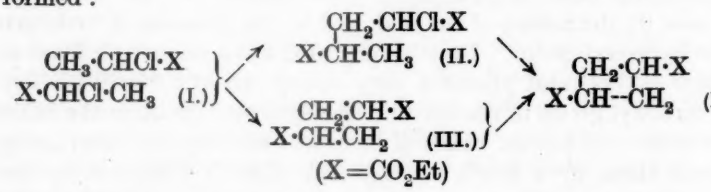
CAMBRIDGE. [*Received, September 14th*, 1925.]

CCCLXXXII.—*The Possible Enhanced Activity of Newly-formed Molecules.*

By FRANK ROBERT GOSS and CHRISTOPHER KELK INGOLD.

IN the course of investigations carried out during the past few years, the authors have frequently been unable to confirm an apparently obvious reaction mechanism by preparing the supposed intermediate products and subjecting them to the conditions of the original experiment; the substances either remained unaltered or behaved differently from expectation. Similar experiences have been recorded by others, and the phenomenon appears sufficiently widespread to give some support for the suggestion that intermediates may be produced in a reactive condition in which they are capable of changes which cannot occur after the energy associated with the formation of the compound has been dissipated. This hypothesis of "nascent molecules" is, of course, not new; but it is one which should be accepted only after conclusive evidence has been furnished, and whilst it is not claimed that the observations recorded in this paper constitute sufficient grounds for embracing so far-reaching a hypothesis, they appear to possess some significance from this point of view.

Two mechanisms suggest themselves for the formation of the *cyclo*butane ester (IV) (Markovnikov and Krestovnikov, *Annalen*, 1880, **208**, 334) from α-chloropropionic ester (I) and sodium ethoxide: the elimination of hydrogen chloride is either inter-molecular, in which case γ-chloro-α-methylglutaric ester (II) is the intermediate product, or intramolecular, ethyl acrylate (III) being first formed:



The chloro-ester (II) has been prepared and subjected to the action of sodium ethoxide under the same conditions. It gave no

detectable quantity of the *cyclo*butane ester, but, on the other hand, yielded the *cyclo*propane ester (V), together with the lactonic ester (VI), the unsaturated ester (VII) and the ethoxy-ester (VIII).

(V.) $H_2C<\begin{matrix}CH\cdot CO_2Et\\ C(CH_3)\cdot CO_2Et\end{matrix}$ $H_2C<\begin{matrix}CH(CO_2Et)\cdot O\\ CH(CH_3)-CO\end{matrix}$ (VI.)

$CO_2Et\cdot CHMe\cdot CH{:}CH\cdot CO_2Et$ (VII.) $CO_2Et\cdot CHMe\cdot CH_2\cdot CH(OEt)\cdot CO_2Et$ (VIII.)

Acrylic ester (III) was treated in a similar manner. Again no *cyclo*butane ester could be detected, but only its unsaturated isomeride, α-methyleneglutaric ester (IX), which was the chief product apart from β-ethoxypropionic ester (X).

(IX.) $CO_2Et\cdot CH_2\cdot CH_2\cdot C(:CH_2)\cdot CO_2Et$ $EtO\cdot CH_2\cdot CH_2\cdot CO_2Et$ (X.)

Although these experiments provide no direct evidence of the intervention either of (II) or of (III) in the series of changes leading to the *cyclo*butane ester (IV), it may not be inappropriate to suggest that if the later change depends on the energy of formation of the intermediate, probably it is acrylic ester that acts in this way; for not only are four-membered rings produced on the whole more easily by additive synthesis than by the closure of a chain, but also the double linking in acrylic ester is more likely to derive temporary activity from its own formation than are the chlorine or methyl-hydrogen atoms of (II) from a reaction in which they are not directly concerned. In this connexion, the suggestion may tentatively be advanced that the double bond in acrylic ester is possibly semi-polar when first produced (which it would be if hydrogen and chlorine were removed from chloropropionic ester, not as atoms, but as ions), although it is undoubtedly non-polar in the ordinary substance (Sugden, Reed, and Wilkins, this vol., p. 1525).

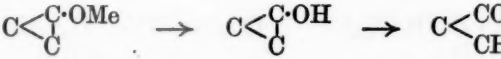
It has been observed (J., 1922, **121**, 1552) that α-campholenic acid (XI) when warmed with an alkaline suspension of silver oxide becomes partly converted into camphor (XIII), and the suggestion was advanced that reduction to dihydrocampholenic acid (XII) first occurred. This reaction has again been investigated and both *cis*- and *trans*-dihydrocampholenic acids have been subjected to similar experimental conditions; both, however, remained unaltered.

$$C_8H_{13}\cdot CH_2\cdot CO_2H \longrightarrow C_8H_{15}\cdot CH_2\cdot CO_2H \longrightarrow C_8H_{14}<\begin{matrix}CO\\ CH_2\end{matrix}$$

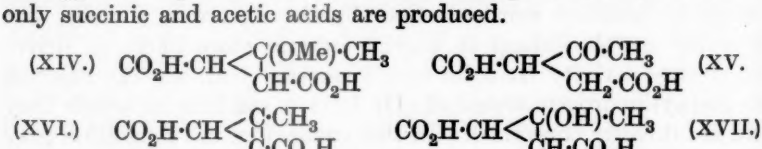
(XI.) (XII.) (XIII.)

Other cases have been observed in connexion with the opening of the *cyclo*propanol ring. It has been shown that methoxy-

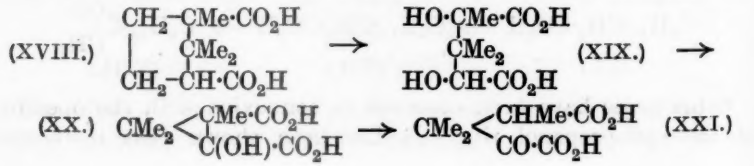
*cyclo*propanes on treatment with demethylating agents yield first *cyclo*propanols, which may undergo further conversion into open-chain ketones, the extent of the latter reaction being limited by its reversibility and the consequent equilibrium, which varies from case to case:



In the case of the methoxy-ring acid (XIV), the corresponding keto-acid is, of course, acetosuccinic acid (XV), which, if acid is used as demethylating agent, passes into lævulic acid with loss of carbon dioxide. It is more remarkable, however, that when concentrated alkali is employed, lævulic acid is still the sole product, although acetosuccinic esters yield mainly succinic and acetic acids, and only a small proportion of lævulic acid, under these conditions. On the other hand, if alkali of the same strength is used to open the ring in the *cyclo*propene acid (XVI)—a reaction which, in view of the known tendency of glutaconic acids to add on water in the presence of alkalis, giving β-hydroxy-acids (*e.g.*, XVII), can scarcely be supposed to proceed otherwise than through acetosuccinic acid—only succinic and acetic acids are produced.



Whilst the mechanism formulated below has been established as the most probable one for the formation of Balbiano's acid (XXI) from camphoric acid (XVIII) by oxidation, Pandya and Thorpe (J., 1923, **123**, 2858) synthesised the intermediate hydroxy-ring acid (XX) but could not convert it into Balbiano's acid. Although working with other ends in view, they were struck by this and suggested that the real intermediary was the opposite stereo-isomeride to that which they had synthesised; it can, however, readily be seen from models that the intervening hydroxy-acid should possess precisely the configuration of the acid which Pandya and Thorpe synthesised and found unreactive. Other similar instances involving the failure of a ring to open have been recorded from time to time and some of these are now under investigation.



Experimental.

Action of Sodium Ethoxide on Ethyl α-Chloropropionate.—Ethyl α-chloropropionate, prepared from pure, dry lactic acid (Brühl, *Ber.*, 1876, **9**, 35), was treated with sodium ethoxide as described by Markovnikov and Krestovnikov (*loc. cit.*) and by Haworth and Perkin (J., 1898, **73**, 336). To 20 g. of the ester at 80°, dry sodium ethoxide (10 g.) was added in small portions; the temperature was finally kept at 100° for 3 minutes, and after cooling the product was poured into dilute acid and isolated by extraction with ether. As stated by Markovnikov and Krestovnikov, it consisted mainly of ethyl α-ethoxypropionate, b. p. 50°/4 mm. This was converted into its amide, which melted at 63° after crystallisation from petrol (b. p. 40—60°) and was identified with that described by Wurtz (*Ann. chim.*, 1860, **59**, 174) (Found: C, 50·9; H, 10·0. Calc., C, 51·2; H, 9·5%). The remainder (about 10%) of the product, b. p. 120°/4 mm., consisted of the *cyclo*butane-1 : 3-dicarboxylic ester, which was converted by hydrolysis into the corresponding acid, m. p. 170°, as described by Markovnikov and Krestovnikov.

Action of Sodium Ethoxide on Ethyl α-Chloro-γ-methylglutarate.—Ethyl α-chloro-γ-methylglutarate (this vol., p. 393) was prepared by treating the lactone of ethyl α-hydroxy-γ-methylglutarate with phosphorus pentachloride and pouring into alcohol. The decomposition with sodium ethoxide (12 g. and 40 g. of the ester) was carried out as described above, and the product was completely hydrolysed. The acids were digested for some days with an aqueous suspension of precipitated calcium carbonate, and the filtered solution was concentrated and allowed to crystallise; the calcium salt of the *trans-cyclo*propane acid (m. p. 168°) then separated. The filtrate from the calcium salts was worked up for organic acids, which were converted through their silver salts into benzyl esters. The portion of these boiling below 240°/15 mm. yielded the original lactone on hydrolysis. By distillation at 1 mm. the less volatile esters were separated into a small preliminary fraction from which on hydrolysis α-methylglutaconic acid together with a liquid acid (probably the ethoxy-acid described below) was obtained, and a fraction (32 g.), b. p. 230—260°, which on hydrolysis gave a liquid consisting, as analysis indicated, mainly of the ethoxy-acid. This was purified by careful distillation of the *ethyl* ester, b. p. 126—129°/12—14 mm. (Found: C, 58·1; H, 9·0. $C_{12}H_{22}O_5$ requires C, 58·5; H, 8·9%); the liquid *acid* was recovered by hydrolysis (Found: C, 50·2; H, 7·5. $C_8H_{14}O_5$ requires C, 50·5; H, 7·3%).

Action of Sodium Ethoxide on Ethyl Acrylate.—Ethyl acrylate was prepared from ethyl αβ-dibromopropionate by Röhm's method

(*Ber.*, 1901, **34**, 573). The reaction was carried out exactly as described in the case of ethyl α-chloropropionate, except that for 20 g. of ester 15 g. of sodium ethoxide were employed. The products were isolated in an identical manner and again consisted to the extent of nine-tenths of a liquid distilling at 50°/4 mm. and one-tenth of a liquid distilling at 120°/4 mm. The former was shown to be ethyl β-ethoxypropionate (compare Purdie and Marshall, J., 1891, **59**, 475) by conversion into the corresponding amide described by Kilpi (*Z. physikal. Chem.*, 1912, **80**, 184), which was crystallised from water; m. p. 50° (Found: C, 50·6; H, 10·1. Calc. for $C_5H_{11}O_2N$, C, 51·2; H, 9·5%). The high-boiling fraction consisted of ethyl α-methyleneglutarate and yielded on hydrolysis the corresponding acid, m. p. 130° (Röhm, *Ber.*, 1901, **34**, 427).

α-Campholenic Acid and α-Campholenamide.—*dl*-Campholenonitrile, b. p. 100°/5 mm., was prepared by the method of Tiemann (*Ber.*, 1895, **28**, 2167) from *d*-camphoroxime, and obtained in 75% yield. It was converted into a mixture of the acid and amide by boiling 3 g. with a solution of 5 g. of potassium hydroxide in 25 c.c. of ethyl alcohol. Addition of water precipitated the amide, m. p. 122°, and more was obtained by extracting the filtrate. The acid extracted after acidification of the mother-liquor distilled at 137°/1 mm.

α-Campholanic Acid.—The *cis*-acid was prepared by the reduction of α-campholenic acid with hydrogen and platinum black (Lipp, *Ber.*, 1922, **55**, 1883). It was distilled at 140°/1 mm.

The *trans*-acid was obtained by reducing α-campholenamide in the same way (*loc. cit.*) and hydrolysing the α-campholanamide first formed by boiling for 50 hours with 3 g. of potassium hydroxide in 15 c.c. of alcohol. The acid was distilled at 141°/1 mm.

Action of Silver Oxide on α-Campholenic Acid and α-Campholanic Acid.—α-Campholenic acid and *cis*- and *trans*-α-campholanic acids were added in separate experiments to a suspension of 2·5 g. of silver oxide in a solution of 0·5 g. of calcium oxide in 25 c.c. of water. In the experiment with α-campholenic acid, the silver oxide was rapidly reduced and the amount of camphor deposited in the condenser reached a maximum after 4 hours' heating. The saturated acids, however, gave no trace of camphor under similar conditions even after several days, and the silver oxide remained apparently unaltered.

Action of Hydrochloric Acid on 3-Methoxy-3-methylcyclopropane-1:2-dicarboxylic Acid.—The acid, prepared as described by Goss, Ingold, and Thorpe (J., 1923, **123**, 3358; this vol., p. 468), was boiled for 2 hours with ten times its weight of 20% hydrochloric acid. From the product a quantitative yield of lævulic acid was

obtained, which was identified by direct comparison and through its semicarbazone and phenylhydrazone, the m. p.'s of which were not depressed by admixture with genuine specimens of the respective substances. The lactone of 3-hydroxy-3-methyl*cyclo*propane-1 : 2-dicarboxylic acid was unaffected by this treatment.

Action of Potassium Hydroxide on 3-*Methoxy*-3-*methyl*cyclo*propane*-1 : 2-*dicarboxylic Acid.*—The acid was boiled for 30 minutes with 64% aqueous potassium hydroxide. From the cooled solution ether extracted lævulic acid, which was identified as described above. The lactone of 3-hydroxy-3-methyl*cyclo*propane-1 : 2-dicarboxylic acid was unaffected by the same treatment.

Action of Hydrobromic Acid on the Methoxy-acid : Formation of 3-*Methyl*-Δ^2-cyclo*propene*-1 : 2-*dicarboxylic Acid.*—The methoxy-acid was boiled for 1 hour with 20 parts by weight of concentrated hydrobromic acid, and the resulting solution was diluted and extracted with ether, methyl*cyclo*propenedicarboxylic acid being obtained.

Action of Potassium Hydroxide on 3-*Methyl*-Δ^2-cyclo*propene*-1 : 2-*dicarboxylic Acid.*—(1) The ring-acid was boiled for 2 minutes with 55% aqueous potassium hydroxide, and the solution was cooled, strongly acidified, and extracted with ether. Unchanged material was recovered.

(2) The experiment was repeated, the time being increased to 30 minutes. The product consisted of a mixture of the *cyclo*propene acid and succinic acid, which were separated by fractional crystallisation and identified by direct comparison.

(3) The ring-acid was boiled for 2 minutes with 64% potassium hydroxide. On working up for acids, a mixture of the *cyclo*propene acid and succinic acid was obtained.

(4) The above experiment was repeated, the time being increased to 30 minutes. The solid product consisted solely of succinic acid. Acetic acid also was produced, but this was detected by qualitative tests only and was not purified.

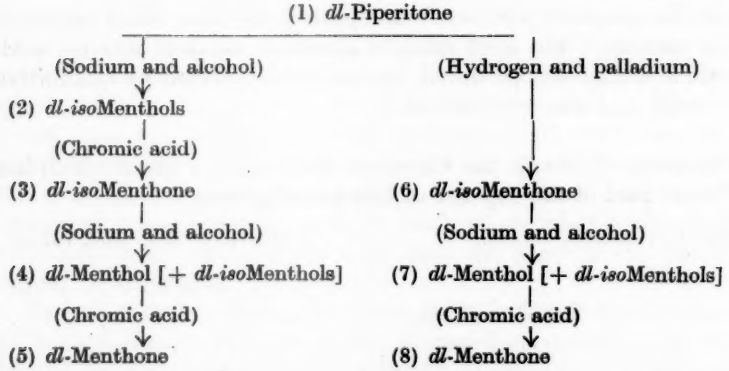
We desire to thank the Chemical Society for a grant which has defrayed part of the expense of this investigation.

THE UNIVERSITY, LEEDS. [*Received, May 21st*, 1925.]

CCCLXXXIII.—*Researches in the Menthone Series. Part I.*

By JOHN READ and ALISON MARY RITCHIE COOK.

THE information hitherto available respecting *dl*-menthone is derived mainly from the work of Pickard and Littlebury on the catalytic reduction of thymol (J., 1912, **101**, 109) and a note by Wallach on the catalytic reduction of synthetic *dl*-Δ^1-*p*-menthen-3-one (*Annalen*, 1913, **397**, 217). It is questionable whether a pure specimen of *dl-iso*menthone had been prepared and recognised as such prior to the work of Hughesdon, Read, and Smith on the reduction of piperitone (J., 1923, **123**, 2916). The "inactive menthone" prepared by Wallach gave the semicarbazone (m. p. 212°) characteristic of *dl-iso*menthone, whilst the derived oxime (m. p. 79—80°) corresponded with *dl*-menthone. These and other apparent inconsistencies in the literature of the subject have now been satisfactorily explained, and it has been found possible to convert *dl*-piperitone at will into derivatives of either series. Alkaline reduction of *dl*-piperitone (1, below) yields a mixture of liquid and solid menthols, in which it has not proved possible to detect *dl*-menthol or *dl-neo*menthol; a preliminary examination of the menthols concerned indicates that they are derived from *dl-iso*menthone rather than from *dl*-menthone. By means of the operations summarised below, this material was transformed successively to *dl-iso*menthone (3), *dl*-menthol (4), and *dl*-menthone (5). In a further series of operations (6, 7, and 8) a more direct passage from *dl*-piperitone to *dl-iso*menthone and *dl*-menthone was secured:



The relationships may be explained on the basis of the establishment of definite dynamic equilibria between *iso*menthone and

menthone in the presence of alkali and under other influences. The main product of the alkaline reduction of *dl-iso*menthone is *dl*-menthol, which may be separated to a large extent in the crystalline form from the associated liquid material. The latter is probably composed largely of *dl*-menthol, accompanied by a liquid mixture of *dl-iso*menthols. From the above considerations it is clear that by repeated oxidation and reduction this liquid by-product may be used as a source of further quantities of crystalline *dl*-menthol. When *dl*-menthol is oxidised by chromic acid in the final operation it yields practically pure *dl*-menthone, which shows little tendency to isomerise into *dl-iso*menthone in the presence of this reagent. By treating the resulting *dl*-menthone with alcoholic alkali, however, it may be transformed into the equilibrium mixture of *dl*-menthone and *dl-iso*menthone. Through the careful avoidance of disturbances due to the use of alkaline reagents it has been possible to prepare a number of pure derivatives of *dl*-menthone and *dl-iso*menthone, the melting points of which are indicated in the following summary:

Derivative.	*dl-iso*Menthone.	*dl*-Menthone.	Wallach's value.
Oxime	99—100°	81—82°	79—80°
Benzoyloxime	55·5	72—73	69—70
*iso*Oxime.....	94—95	114—115	87—88
Semicarbazone (α)	225	185—186	219
,, (β)	177—178	161	—

The melting points of the semicarbazones of *dl-iso*menthone were observed by Hughesdon, Smith, and Read (*loc. cit.*). The values quoted in the last column suggest that the "inactive menthone" described by Wallach (*loc. cit.*) consisted of *dl-iso*menthone, from which the oxime was prepared in an alkaline medium. *dl-iso*-Menthoneoxime is remarkable by reason of its capacity for forming well-developed crystals, so that for the first time it becomes possible to submit a menthoneoxime to a complete goniometric examination. *dl*-Menthone and *dl-iso*menthone may most readily be discriminated by preparing the oximes or semicarbazones in weakly acid solutions.

Up to the present, attempts to reduce piperitone to menthol or menthone in an acid medium have been unsuccessful, the ketone being practically unaltered by such reagents as tin and concentrated hydrochloric acid or zinc dust and glacial acetic acid. Distinct evidence was obtained of the formation of an appreciable amount of *dl*-α-phellandrene during the alkaline reduction of *dl*-piperitone, the relationship being of particular interest in view of the occurrence together of the lævo-modifications of these two substances in various eucalyptus oils.

Experimental.

Products obtained through an Initial Alkaline Reduction of dl-*Piperitone.*—1. The piperitone used throughout this work was extracted from the essential oil of *Eucalyptus dives*, using sodium bisulphite (*J. Soc. Chem. Ind.*, 1923, **42**, 339T).

2. In order to avoid all possibility of the formation of optically active products, the piperitone (40 g.) was racemised by means of alcoholic sodium ethoxide, prior to reduction with sodium and alcohol (J., 1923, **123**, 2270, 2918). Altogether, 880 g. of *dl*-piperitone yielded 820 g. of crude menthol, which was submitted to two systematic distillations under diminished pressure. The first fraction (b. p. to 87°/10 mm.) had an odour similar to that of α-phellandrene: its physical characteristics (J., 1923, **123**, 1660), together with the ready formation of a nitrosite melting at 106—107° and resembling that of *dl*-α-phellandrene, indicated that the fraction consisted essentially of this terpene. A further series of reductions carried out with piperitone which had been carefully freed from phellandrene by two successive fractional distillations under diminished pressure gave a crude product (223 g.) containing 9·1% of a similar fraction with the following physical characteristics: b. p. to 87°/10 mm., $\alpha_D^{16°}$ −1·58° (1-dcm. tube), $n_D^{15°}$ 1·4798. It therefore appears conclusive that *dl*-α-phellandrene is formed to an appreciable extent in the alkaline reduction of *dl*-piperitone. The total yield of menthols was 42·4%.

3. Upon oxidation with chromic acid (*Annalen*, 1889, **250**, 325), a total quantity of 410 g. of the liquid product (b. p. 95—97°/10 mm.) yielded 332 g. of a liquid possessing the characteristic odour of menthone. When distilled twice under diminished pressure, 37% of the product distilled up to 82°/8 mm. ($\alpha_D^{17°}$ −0·18°, $n_D^{17°}$ 1·4553), and 40% at 82—85°/8 mm. ($\alpha_D^{17°}$ −0·34°, $n_D^{17°}$ 1·4571). The latter fraction was used in preparing the derivatives described below, and appeared to consist essentially of *dl-iso*menthone.

4. Upon reduction with sodium and alcohol in the usual manner, a specimen of the *dl-iso*menthone just described (24·7 g.) yielded a product (24·0 g.) which distilled almost completely at 100—105°/15 mm. Three distinct fractions, each boiling over a range of one degree between 102° and 105°/15 mm. and having $n_D^{16°} = 1·4640$, deposited crystalline material on cooling, the liquid becoming permeated in each instance with fine radiating needles reaching a length of 2 cm. When separated and dried on porous plate, the three specimens melted at 32—34° and yielded the characteristic *dl*-menthyl hydrogen phthalate.

5. The menthone obtained by oxidising the crystalline *dl*-menthol

from the preceding operation resembled the product described under (8) below, and thus consisted essentially of *dl*-menthone.

Products obtained through an Initial Catalytic Reduction of dl-*Piperitone*.—6. Carefully purified *dl*-piperitone (50 g.) was hydrogenated at the ordinary temperature, under a pressure of 0·25 atmosphere, in presence of colloidal palladium (J., 1923, **123**, 2921). The mixed yields from four operations, when systematically distilled under diminished pressure, gave a main fraction, b. p. 90—93°/18 mm., $n_D^{18°}$ 1·4580; this was optically inactive and appeared to be practically identical with product (3), thus consisting of *dl-iso*menthone.

7. Upon reducing 18 g. of the preceding product with sodium and alcohol, a yield of 15·5 g. of crude menthol was obtained. This failed to crystallise, but when fractionally distilled the portion passing over at 107—112°/23 mm. (9·3 g.) furnished 2·3 g. of crystals, which possessed the pronounced odour of ordinary menthol and melted at 32—34°. Not only these crystals but also a liquid fraction of somewhat lower boiling point (105—107°/23 mm.; $n_D^{16°}$ 1·4686) yielded the characteristic *dl*-menthyl hydrogen phthalate (Pickard and Littlebury, *loc. cit.*).

8. *dl*-Menthol (m. p. 32—34°; 54 g.) was oxidised with chromic acid in the usual manner, except that the temperature was raised to 70° in order to decompose the black, crystalline chromium compound. The crude product (45·1 g.), when distilled, passed over almost completely at 85—89°/12 mm., and had $n_D^{17°}$ 1·4541. The preparation of the derivatives described below showed it to consist essentially of *dl*-menthone, so that it was identical with product (5) and differed from products (3) and (6). *dl*-Menthone possesses a characteristic peppermint odour, which is if anything even more pronounced than that of *l*-menthone. *dl-iso*Menthone, on the other hand, has a decidedly fainter odour of the same general character.

Derivatives of dl-iso*Menthone*.—dl-iso*Menthoneoxime* was prepared from *dl-iso*menthone (b. p. 82—85°/8 mm.) obtained in preparation (3) above, by treatment in the usual way with hydroxylamine acetate (J., 1922, **121**, 586): 92·4 g. of the ketone yielded 100·4 g. of crude oxime, which crystallised partly when kept for a short time in a vacuum desiccator. The crystalline material (35 g.), dried on porous plate, melted indefinitely between 85° and 90°, but attained a constant m. p., 99—100°, after three recrystallisations from warm light petroleum. The substance is readily soluble in organic solvents, but when pure it crystallises from light petroleum with great ease in magnificent, transparent prisms, distinguished by their high lustre. The crystals were

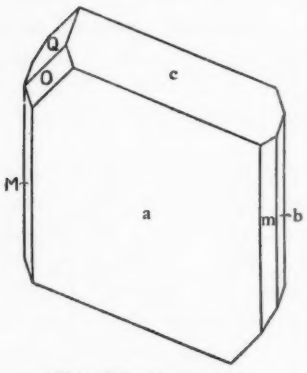
kindly measured by Mr. T. V. Barker, M.A., of the Department of Mineralogy, University of Oxford, who reports that they are anorthic with forms *a*, *m*, *b*, *M*, *c*, *Q*, and rarely *O*, developed in the proportions indicated by Fig. 1. The elements $a : b : c = 2{\cdot}049 : 1 : 1{\cdot}281$; $\alpha = 112°\ 12'$, $\beta = 116°\ 17'$, $\gamma = 86°\ 57'$, were computed from the following results of measurement of four crystals :

	a(100).	*m*(110).	*b*(010).	*M*($\bar{1}$10).	*c*(001).	*Q*(0$\bar{1}$1).	*O*(1$\bar{1}$1).
ϕ ...	0° 0′	0° 0′	0° 0′	0° 0′	*67° 48′	*134° 18′	134° 18′
ρ ...	0 0	56 51(14)	*82 6	*110 17	*62 48	75 23(3)	52 18(20)

Optically the extinction is nearly straight with the vertical edge, and an optic axis lies just within the field (Found : C, 71·1; H, 11·1. $C_{10}H_{19}ON$ requires C, 71·0; H, 11·2%).

The mother-liquors from the recrystallisation of the oxime deposited an oily product when concentrated by evaporation; when kept for some time, this material furnished a further quantity of the crystalline oxime described above, but no other crystalline oxime could be isolated. The lower fraction of *dl-iso*menthone (b. p. to 82°/8 mm.) from preparation (3) behaved similarly when oximated.

Fig. 1.



dl-iso*Menthoneoxime.*

*dl-iso*Menthone prepared by the catalytic reduction of *dl*-piperitone (6) gave a similar product, which, however, furnished a considerably higher proportion of the crystalline oxime. Fractions melting indefinitely between 60° and 75° were obtained from the mother-liquors, but no indication was forthcoming of the presence in these of *dl*-menthoneoxime.

Benzoyl-dl-iso*menthoneoxime* was prepared, by benzoylation in pyridine solution, as a viscid oil which was induced to crystallise with great difficulty. The crude product, after drying on porous plate, melted at 52—54°. After three successive recrystallisations from light petroleum, in which the derivative is very soluble, the melting point became constant at 55·5°, the pure substance separating in massive, transparent prisms suitable for goniometric examination. The product obtained by benzoylating the oily mother-liquor from the crystalline oxime could not be induced to crystallise (Found : C, 74·7; H, 8·9. $C_{17}H_{23}O_2N$ requires C, 74·7; H, 8·8%).

dl-iso*Menthone*iso*oxime*, prepared by dissolving crystalline *dl-iso*menthoneoxime in cold concentrated sulphuric acid (Wallach, *Annalen*, 1894, **278**, 304), crystallised from hot water containing

a little alcohol in fine, glistening needles, m. p. 94—95°. The product of the reaction appeared to be homogeneous (Found: C, 70·2; H, 11·1. $C_{10}H_{19}ON$ requires C, 71·0; H, 11·2%).

Derivatives of dl-*Menthone.*—*dl*-Menthone from preparations (5) and (8) above, when oximated in the manner described for piperitone (J., 1922, **121**, 586), yielded *dl*-menthoneoxime (m. p. 81—82°) associated with a considerable amount of oily material. Unlike the stereoisomeric *dl-iso*menthoneoxime, this derivative could not be obtained in crystals sufficiently well developed for goniometric examination.

Attempts to benzoylate the crystalline oxime by the Schotten-Baumann method gave unsatisfactory results, but by the use of pyridine an oily product was obtained, which after extraction with ether and keeping in a vacuum desiccator crystallised spontaneously. The substance crystallised from light petroleum in small, transparent plates or glistening prisms, m. p. 72—73°. *Benzoyl*-dl-*menthoneoxime* is very soluble in all the usual organic solvents; it does not form such well-developed crystals as benzoyl-*dl-iso*-menthoneoxime (Found: C, 74·7; H, 8·6. $C_{17}H_{23}O_2N$ requires C, 74·7; H, 8·8%). The oily material from the mother-liquor of the crystalline *dl*-menthoneoxime yielded a viscid liquid when benzoylated in pyridine solution.

dl-*Menthone*isooxime, prepared from crystallised *dl*-menthoneoxime in the manner indicated above, crystallised from hot water containing a little alcohol in fine, soft needles, m. p. 114—115°, and was readily obtained pure (Found: C, 69·9; H, 10·9. $C_{10}H_{19}ON$ requires C, 71·0; H, 11·2%).

Upon allowing *dl*-menthone (10·5 g.) to react with semicarbazide in the manner described in a previous paper (J., 1923, **123**, 2920), a crystalline product (10·2 g.) was readily isolated. By continued fractional crystallisation from hot methyl alcohol a small fraction of dl-*menthone*-α-*semicarbazone* was eventually obtained: this forms characteristic and well-defined, glistening prisms, m. p. 185—186° (Found: C, 62·1; H, 10·2. $C_{11}H_{21}ON_3$ requires C, 62·5; H, 10·0%). The bulk of the product, however, consisted of small, glistening needles of dl-*menthone*-β-*semicarbazone*, m. p. 161—162°; this derivative is more soluble than the isomeric compound (Found: C, 62·7; H, 10·3%). No semicarbazone characteristic of *dl-iso*-menthone could be isolated from this product; an intermediate product melting at about 177°, when mixed with *dl-iso*menthone-β-semicarbazone (m. p. 177—178°; J., 1923, **123**, 2922), softened at 158° and melted indefinitely between 169° and 176°. It may be remarked that *dl-iso*menthone-α-semicarbazone (m. p. 225°) is by far the least soluble of the semicarbazones of the optically inactive

menthones; its absence from the above reaction-product thus affords a criterion of the freedom of the specimen of *dl*-menthone from *dl-iso*menthone.

We express our thanks to the Department of Scientific and Industrial Research for a maintenance grant to one of the authors (A.M.R.C.). The investigation is being continued.

UNITED COLLEGE,
UNIVERSITY OF ST. ANDREWS. [*Received, July 6th*, 1925.]

CCCLXXXIV.—*The Ionic Activity Product of Water in Glycerol–Water Mixtures.*

By JAMES COLVIN.

MEASUREMENTS have shown that a very marked increase occurs in the activity of hydrogen ion derived from hydrogen chloride in aqueous solution in the presence of a solvent-displacing agent, generally a non-electrolyte such as sucrose or glycerol (Moran and Lewis, J., 1922, **121**, 1613). It is of interest, therefore, to determine the activities of hydrogen and hydroxyl ions in a solution containing a substance such as glycerol, with a view to obtain the value of the ionic activity product of water, *i.e.*, the product of the hydrogen- and the hydroxyl-ion activities. Should the product remain constant, independent of the concentration of glycerol, it would permit of the determination of hydroxyl-ion activities by the hydrogen electrode, which is in many cases more convenient to use than a direct hydroxyl-ion electrode, such as the Donnan–Allmand electrode.

Measurements of the activities of hydrogen and hydroxyl ions were therefore carried out in solutions of $N/100$-sodium hydroxide, containing various amounts of glycerol.

EXPERIMENTAL.

The sodium hydroxide solution was prepared from metallic sodium and water free from carbon dioxide. The glycerol had been previously employed for conductivity measurements. For the measurements of the *E.M.F.* of the cells, a Cambridge–Paul potentiometer, reading to 0·1 millivolt, was used in conjunction with a mirror galvanometer. To avoid stray currents, the potentiometer and galvanometer were mounted on glass, insulated from earthed iron sheets by paraffin wax. The cells were maintained in a thermostat at a temperature of $25° \pm 0·05°$.

The Activity of Hydrogen Ion in Aqueous Solutions of Sodium Hydroxide and Glycerol.—The cell employed was of the following type :

$$- \begin{matrix}\text{Pt}\\ \text{H}_2\end{matrix} \Big| \begin{matrix}N/100\text{-NaOH}\\ \text{Glycerol}\end{matrix} \Big| \text{Sat. KCl} \Big| N\text{-Calomel} \Big| +$$

The electrode consisted of platinum foil, coated with platinum black, and was placed for 10 minutes in boiling water before use, following the procedure of Allmand (J., 1909, **95**, 2151). The hydrogen gas was prepared by the electrolysis of a solution of caustic soda and was washed by passing through a wash-bottle containing the solution under investigation. The gas thus being saturated with water vapour at the same pressure as the vapour pressure of the solution in the cell, no concentration changes could occur in the solution due to evaporation.

As some doubts have been expressed as to the trustworthiness and reproducibility of the hydrogen electrode in alkaline solution, it was thought advisable to carry out some preliminary measurements on the cell,

$$- \begin{matrix}\text{H}_2\\ \text{Pt}\end{matrix} \Big| N/10\text{-NaOH} \Big| \text{Sat. KCl} \Big| N\text{-Calomel} \Big| +$$

The following results were obtained :

Cell	1	2	3	4	5	6
E.M.F. (volts)	1·0412	1·0415	1·0411	1·0412	1·0415	1·0411

The mean value of the *E.M.F.*, 1·0413 volts, is in satisfactory agreement with the value, 1·0416 volts, obtained by Harned (*J. Amer. Chem. Soc.*, 1916, **37**, 2460).

As the reproducibility of the hydrogen electrode was thus satisfactorily demonstrated, measurements were made, using $N/100$-sodium hydroxide in presence of various amounts of glycerol. As the quantity of glycerol in the solution increased, a longer time was required for the electrode to attain equilibrium; in all cases, however, the values could be reproduced. The activities of the hydrogen ion were calculated by means of the formula $\pi_{H\cdot} = 0{\cdot}282 + 0{\cdot}059 \log_{10} a_{H\cdot}$. The absolute potential of the calomel electrode was taken to be 0·56 volt at 18°. The temperature coefficient of the electrode is 0·00068 volt per degree, hence the value at 25° is 0·5648 volt (compare Chroustchov and Sitnikov, *Compt. rend.*, 1889, **108**, 941).

The results obtained are in Table I.

The glycerol produces a very marked increase in the activity of hydrogen ion in the solution of alkali.

TABLE I.

G. of glycerol per 100 c.c.	*E.M.F.* in volt.	$-\pi_{H'}$.	$a_{H'} \times 10^{12}$.
0·0	0·9870	0·4222	1·16
12·6	0·9661	0·4013	2·62
20·0	0·9580	0·3932	3·60
25·2	0·9530	0·3882	4·40
40·0	0·9406	0·3758	7·06

The Activity of Hydroxyl Ion in Aqueous Solutions of Sodium Hydroxide and Glycerol.—The electrode employed was that described by Donnan and Allmand (J., 1911, **99**, 845) and consists essentially of a layer of mercuric oxide superimposed on a layer of mercury, the electrode vessel then being filled with the solution under investigation. The electrode reaction is given by the equation

$$HgO + H_2O + 2E = Hg + 2OH',$$

so that the equation for the electrode potential becomes

$$\pi_{OH'} = E'_0 - \frac{RT}{2F} \log \frac{a_{Hg} \times a^2_{OH'}}{a_{HgO} \times a_{H_2O}},$$

where E'_0 is the electrode potential in solutions where all the activities are equal to unity. Since the activities of the mercury and solid mercuric oxide are constant, they may be included in the first term on the right-hand side. For dilute solutions, the activity of the water remains sensibly constant. Hence the equation for the electrode potential in dilute solutions may be written

$$\pi_{OH'} = E_0 - 0{\cdot}059 \log_{10} a_{OH'}.$$

The value of the term E_0 was determined experimentally by the following method. The *E.M.F.* of the cell

$$- \text{Hg, HgO} \;\big|\; N/10\text{-KOH} \;\big|\; \text{Sat. KCl} \;\big|\; N\text{-Calomel} \;\big|\; +$$

was found to be 0·1178 volt at 25°. This gives the value 0·4470 volt as the electrode potential in $N/10$-potassium hydroxide. The activity of hydroxyl ion in the solution can be obtained from the data of Knobel (*J. Amer. Chem. Soc.*, 1923, **45**, 70) for the mean activity of potassium hydroxide in aqueous solution. On the assumption that the potassium ion has the same activity in solutions of potassium hydroxide and of potassium chloride of the same concentration, by employing the data of Noyes and MacInnes (*J. Amer. Chem. Soc.*, 1920, **42**, 239) for the activity of potassium ion in potassium chloride solutions, the value 0·0825 is obtained for the activity of hydroxyl ion in $N/10$-potassium hydroxide. By putting this value in the expression for the electrode potential, the value 0·3823 volt is obtained for E_0.

When glycerol is present, however, it is no longer justifiable to equate the activity of the water to unity. The expression for the electrode potential becomes

$$\pi_{OH'} = E_0 + (0{\cdot}059/2) \log_{10} a_{H_2O} - 0{\cdot}059 \log_{10} a_{OH'},$$

in which E_0 has the value found above.

Measurements with the Donnan–Allmand Electrode.—The mercury used in the cells was distilled in a vacuum. The mercuric oxide was prepared by heating the nitrate until no more brown fumes were evolved. The nitrate itself was prepared by acting on redistilled mercury with nitric acid (*d* 1·2) and recrystallising from nitric acid. The product thus obtained gave very reproducible results.

At first a large electrode vessel was used, but was soon discarded in favour of a smaller type, as equilibrium was then more readily attained. The cells set up were of the type

$$- \text{Hg, } \underset{g}{\text{H}_2\text{O}} \;\Big|\; \begin{matrix} N/100\text{-NaOH} \\ \text{Glycerol} \end{matrix} \;\Big|\; \text{Sat. KCl} \;\Big|\; N\text{-Calomel} \;\Big|\; +$$

In all cases, readings of the *E.M.F.* were taken at intervals of 24 hours from the time of setting up the cell. In general, with *N*/100-sodium hydroxide alone present, equilibrium was attained within 48 hours. With glycerol present, the *E.M.F.* declined with time, hence a series of readings taken at intervals of 24 hours for the first 3 days were averaged to give the *E.M.F.* of the cell. As five cells for each concentration of glycerol were set up and the readings averaged, considerable confidence is placed in the results, which are in Table II. The activity of the water in glycerol–water mixtures may be obtained from the vapour pressure data of Perman and Price (*Trans. Faraday Soc.*, 1912, **8**, 74) at 70°. The activity of the water, which may be taken as the ratio of the vapour pressure of the solution to the vapour pressure of the solvent, is regarded as independent of the temperature (Lewis and Randall, "Thermodynamics," p. 349).

TABLE II.

G. of glycerol per 100 c.c.	*E.M.F.*	$\pi_{OH'}$.	a_{H_2O}.	$a_{OH'} \times 10^2$.
0	0·0604	0·5044	1·00	0·883
12·6	0·0394	0·5254	0·98	0·373
20·0	0·0314	0·5334	0·96	0·270
25·2	0·0266	0·5382	0·94	0·221
40·0	0·0147	0·5501	0·89	0·135

The glycerol produces a marked decrease in the activity of the hydroxyl ion.

The Ionic Activity Product of Water.—Sufficient data have now been obtained to calculate the ionic activity product and also the dissociation constant of water in presence of glycerol. The results are in Table III.

TABLE III.

G. of glycerol per 100 c.c.	$a_{H^+} \times 10^{12}$.	$a_{OH'} \times 10^{2}$.	a_{H_2O}.	$a_{H^+} \times a_{OH'} \times 10^{14}$.	$\frac{a_{H^+} \times a_{OH'} \times 10^{14}}{a_{H_2O}}$
0	1·16	0·883	1·00	1·02	1·02
12·6	2·62	0·373	0·98	0·98	1·00
20·0	3·60	0·270	0·96	0·97	1·01
25·2	4·40	0·221	0·94	0·97	1·03
40·0	7·06	0·135	0·89	0·95	1·07

The value of the dissociation constant of water, *i.e.*, $a_{H^+} \times a_{OH'}/a_{H_2O}$, remains practically constant over the whole range up to 40% of glycerol, the deviations from constancy being very small in comparison with the changes in the activities of the individual ions. At the same time, since the changes in the activity of the water effected by the presence of the glycerol are relatively small, the ionic activity product of the water maintains a reasonably constant value.

Summary.

1. Electrometric measurements of the activities of hydrogen ion in aqueous solutions of sodium hydroxide in presence of glycerol have been made at 25°.

2. The Donnan–Allmand electrode has been used to determine the activity of hydroxyl ion in solutions of sodium hydroxide containing glycerol.

3. The dissociation constant of water remains constant for the solutions containing up to 40% of glycerol; the ionic activity product does not exhibit appreciable change over the same range.

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CCCLXXXV.—*A Comparison of Methods of Measuring the Polarity* of Surfaces.*

By Neil K. Adam, Robert S. Morrell, and Ronald G. W. Norrish.

"Polarity" has been recently measured by Norrish (J., 1923, **123**, 3006), the measure being the catalytic activity of the surface for the combination of ethylene and bromine. Another measure of polarity is the attraction of a surface for water, or the work, W, required to separate the surface from water in contact with it; W is related to the angle of contact, θ, of water with the solid surface by the relation

$$W = T(1 + \cos\theta),$$

T being the surface energy of water (Adam and Jessop, this vol., p. 1863). Yet another indication of polarity is the objectionable property which some oil varnishes possess of condensing water on the varnished surface in a moist atmosphere and 'blooming.' Varnished surfaces which bloom easily may be considered more polar than non-blooming surfaces. This paper is an attempt to elucidate the nature of the "polarity" by comparing the results of the different methods of measurement.

Glass, stearic acid, paraffin wax, two non-blooming varnishes, A and B, and one blooming varnish, C, were compared. The non-blooming varnish film was composed of a hard copal resin incorporated in linoxyn containing lead and manganese catalysts. The blooming varnish film contained a rosin ester in tung oil "oxyn," with a manganese catalyst. Both for angle of contact and for catalysis measurements, the varnish was coated on glass and allowed to dry in a current of air (5 litres per hour) at 40—55° until constant in weight. The volatile thinners of the varnishes were expelled and the drying oils oxidised as completely as possible.

In the tables, k is the initial velocity coefficient, k' gives the catalytic effect in terms of k expressed as percentage of the value for glass, θ and W (ergs per sq. cm.) are defined above, and W' is the attraction for water as percentage of the attraction of water

* The terms "polar" and "non-polar" have become general in the sense that "polar" is applied to substances (and to groups therein) which tend to dissolve in water, and "non-polar" to those which dissolve in hydrocarbon solvents. This broad distinction of groups into two classes is a most useful working hypothesis for many investigations, and a more definite understanding of its nature and causes is much needed. The term "polarity" is here used in this sense, leaving entirely open the question whether there exists any resemblance to physical objects of unsymmetrical field of force, such as bar-magnets.—N. K. A.

for itself. The angle of contact method will not detect attractions for water greater than that of water for itself, attractions equal to and greater than this giving zero angle. Glass has an attraction for water at least as great as that of one water surface for another.

Catalytic action measured on dry ethylene and bromine.

Surface.	k.	k'.	θ.	W.	W'.
Glass	0·051	100	0°	not less than 146	100
Varnish A	0·048	94	95	66·6	45·5
Varnish C	0·112	220	60	109·5	75
Paraffin wax	0·003	6	105	54	37
Stearic acid	0·086	168	100	60·5	41

Catalytic action measured on moist ethylene and chlorine.

Glass	$9{\cdot}7\times10^{-4}$	100	0	146	100
Varnish B	4·0 „	41	95	66·6	45·5
Varnish C	11 „	113	65	104	71
Paraffin wax	0·01 „	0·1	105	54	37

The angle of contact measurements were made as described by Adam and Jessop, and are accurate to about 5°. The velocity coefficients for the ethylene–bromine reaction were determined as described by Norrish, fairly good constancy being obtained for the first five minutes of reaction. Ethylene and chlorine in the moist condition were employed for the second series, as it has been found possible thus to obtain more reproducible results than with dry ethylene and bromine; but owing to the higher pressure used there was appreciable attack of the varnish surfaces by the chlorine, which impaired the constancy of the velocity 'constants.' Details of the ethylene–chlorine method will be published shortly. The values, calculated as bimolecular coefficients, are given for the first two minutes of reaction, and afford a comparison of catalytic activity adequate for the present purpose. The figures for reaction rates are, of course, not comparable between the two series.

The angle of contact measurements were taken on the varnishes within a minute or two of immersion in the water. If allowed to soak, these surfaces gave an angle lower by 10° or, in some cases, 20°, the effect of soaking being more marked the greater the angle of contact.

Evidently the attractions for water parallel the veiling properties of the varnishes. It appears that if the attraction is more than about 70% of that of water for itself, the varnish veils; if less than 45 to 50%, it does not veil. We attempted also to grade varnishes in respect of their veiling properties by angle of contact measurements, but owing to the effect of soaking in water, these could not be made sufficiently accurately to distinguish varnishes with a

slight tendency to veil from non-veiling varnishes. The varnishes which were found to be more polar by the angle of contact method were also more polar by the catalytic measure.

There is, however, considerable disagreement between the polarities of the surfaces of different kinds as measured by the catalytic method and by angle of contact. Glass has less catalytic power than either stearic acid or the veiling varnishes, but very much greater attraction for water; and stearic acid, which has only a very slightly greater attraction for water than paraffin wax, has enormously greater catalytic activity. It would, of course, be possible to ascribe the difference to the " polarity " which causes attraction for water being of a different kind from that which confers catalytic activity; but such an *ad hoc* assumption would be particularly unreasonable, as it is not improbable that water itself is concerned in the catalysis. Adam and Jessop concluded that the evidence of angle of contact measurements on long-chain compounds pointed to the polar groups in stearic acid being buried in the interior. Hence it appears that in the catalytic measurements the reacting gases penetrated the surfaces to a short distance. The nature of the oxidised varnish surfaces is unknown: we consider it possible that ethylenic linkings are present. In this way it would be possible for the stearic acid and varnish surfaces to present more catalytically active groups than a glass surface, which must be presumed practically impermeable to the gases. By penetrating the solid to a depth of only the length of a few molecules, it would be possible for the gases to reach more polar groups than are to be found on an equal area of glass. If this is the correct explanation, it involves the assumption that the depth of the ' surface ' is much greater for the catalysis than for the angle of contact measurements. Varnishes differ in their absorption of, and permeability to, water, and no doubt to gases also; but we have not data enough to attempt a prediction of catalytic activity for different varnished surfaces, taking this factor into account. This factor of permeability requires further investigation; in Adam and Jessop's paper some evidence was given that there is more depth involved in the case of crystal flakes of the long-chain amine hydrochlorides than with the other long-chain aliphatic substances used. Nevertheless we feel that, qualitatively, it supplies an adequate reason for the difference in behaviour of different ' surfaces ' to reagents.

Paraffin wax is not a catalyst, because no matter how far the gases may diffuse into the interior, no polar groups are encountered.

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CCCLXXXVI.—*An Electrometric and a Phase Rule Study of some Basic Salts of Copper.*

By Hubert Thomas Stanley Britton.

This paper deals with experiments made to ascertain which of the many basic sulphates and chlorides of copper are definite compounds. Basic sulphates have been reported ranging in composition from $2CuO,SO_3$ to $15CuO,SO_3$, with varying water contents. Pickering (J., 1910, **97**, 1851) regarded the latter as a complex salt of orthosulphuric acid and bivalent and what he supposed to be quadrivalent copper atoms, and Noyes (*J. Amer. Chem. Soc.*, 1916, **38**, 1947) suggested that $3CuO,SO_3,2H_2O$ might be the dihydrated cupric salt of the same acid. The basic chlorides which have been described contain from 1 to 4·5 atoms of copper for each atom of chlorine. Naturally occurring basic sulphates and chlorides are langite, $4CuO,SO_3,4H_2O$; brochantite, containing from 3 to 4 mols. of CuO for 1 mol. of SO_3, together with varying amounts of water, and atacamite, $4CuO,2HCl,3H_2O$—the number of molecules of water varying from 2 to 5.

Bell and Taber (*J. Physical Chem.*, 1908, **12**, 171) and Young and Stearn (*J. Amer. Chem. Soc.*, 1916, **38**, 1947), who studied the basic sulphates of copper from the point of view of the phase rule, obtained very conflicting results and were unable to prove the existence of a definite basic sulphate; doubtless because they used substances which approached equilibrium very slowly.

It has long been known that an amorphous, blue precipitate, agreeing very closely in composition with $4CuO,SO_3,4H_2O$, is produced by treating copper sulphate solution with an insufficiency of alkali (Kane, *Ann. Chim. Phys.*, 1839, **72**, 270; Smith, *Phil. Mag.*, 1845, **23**, 501; Field, *ibid.*, 1862, **24**, 124). Williamson (*J. Physical Chem.*, 1923, **27**, 790) analysed the precipitates obtained by treating molar solutions of copper sulphate with different quantities of alkali. Pickering showed (*Chem. News*, 1883, **47**, 181) that between 1·4 and 1·5 equivalents of potassium hydroxide completely precipitated the copper and that the amount precipitated at any stage of the reaction was directly proportional to the amount of alkali added. He also found a temporary alkalinity to phenolphthalein when 1·5 equivalents of alkali had been added. Similar observations were made by the author, using the oxygen electrode (this vol., p. 2152).

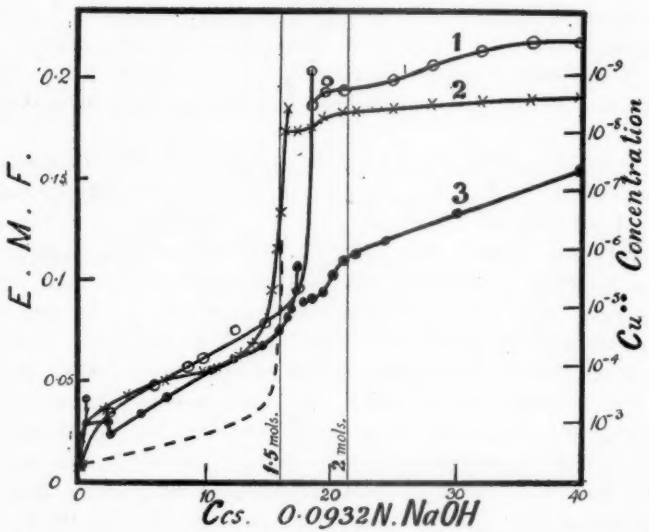
Apart from the little recorded by Kenrick and Lash Miller (*Trans. Roy. Soc., Canada*, 1901, **7**, iii, 35), no systematic work has been done on basic cupric chloride. The precipitate formed

when $N/5$-copper chloride solution was treated at 85° with $N/5$-potassium hydroxide until all the copper had been precipitated had the formula $CuCl_2,3CuO,2H_2O$.

Experimental.

In order to study the mode of precipitation of copper sulphate by sodium hydroxide, electrometric titrations with a copper electrode were carried out. A copper wire electrode, fused into a glass tube, was completely immersed in 100 c.c. of $M/100$-copper sulphate solution, which was connected through a saturated solution of potassium chloride to a normal calomel electrode. The

Fig. 1.



E.M.F.'s between the copper and the calomel electrodes were measured by means of a potentiometer and a capillary electrometer. The electrode was about 2 mm. in diameter and was covered with finely divided copper, deposited electrolytically from $N/10$-copper sulphate solution. That electrodes so prepared worked satisfactorily in copper sulphate solution will be seen from the following measurements. At 20°, the *E.M.F.* of the cell $Cu \mid 0{\cdot}01M\text{-}CuSO_4 \mid$ saturated $KCl \mid N$-calomel was $-0{\cdot}006$ volt. Therefore $E_h\ Cu \mid 0{\cdot}01M\text{-}CuSO_4 = +0{\cdot}283 - 0{\cdot}006 = 0{\cdot}277$ volt. $0{\cdot}01M$-Copper sulphate being taken as 54·7% dissociated ($\Lambda_\infty = 114$, and $\Lambda_{0{\cdot}01M} = 62{\cdot}4$), $0{\cdot}277 = EP_{Cu_h} + 0{\cdot}029 \log 0{\cdot}00547$. Whence $EP_{Cu_h} = 0{\cdot}343$, which is in agreement with the recent value of Jellinek and Gordon (*Z. physikal. Chem.*, 1924, **112**, 214).

Three typical titration curves are given in Fig. 1. The cupric-

ion concentration scale was calculated from the formula $E_{obs.} = -0{\cdot}060 - 0{\cdot}029 \log [Cu^{\cdot\cdot}]$. The dotted line gives the theoretical change in copper-ion concentration calculated on the assumption that $4CuO,SO_3$ alone is precipitated. Curves 1 and 2, plotted from results obtained with an electrode having a thin coating of copper (deposited during 5 minutes' electrolysis), and curve 3 (electrode heavily coated during 1 hour's electrolysis) show that the electrodes became untrustworthy as soon as a precipitate appeared. Deduced from the curves, the values for the concentrations during precipitation are much too small and those for the concentrations when precipitation was complete and the solutions had become alkaline are obviously too large. High *E.M.F.*'s were obtained immediately precipitation was complete, but these fell in the course of 5 minutes to more or less steady values. The effect of the heavy deposit (curve 3) was to render the electrode even more irregular, as may be seen from the second portion of the curve.

The curves show that sudden changes in copper-ion concentration occurred when 1·73 (curve 1), 1·5 (curve 2), and 1·63 equivalents (curve 3) of sodium hydroxide had been added. In titration 2, the alkali was added very slowly, and the mixture was stirred until any green, gelatinous precipitate which might have formed had become pale blue and apparently amorphous. In the other two titrations the alkali was added more rapidly and, although the reactants were thoroughly mixed, stirring was not maintained until the precipitate appeared to have become homogeneous. These experiments show once again that the nature of the precipitate obtained depends on the manner in which the alkali is added. Rapid addition necessitated the use of a larger quantity for complete precipitation and consequently the gelatinous precipitate obtained was more basic than the blue, amorphous * precipitate produced on careful addition of the alkali. This is the reason why Harned (*J. Amer. Chem. Soc.*, 1917, **39**, 252) required in his similar titration of copper sulphate solution six-sevenths of the theoretical quantity of the alkali.

The Anomalous Behaviour of Copper Electrodes in Presence of Copper Hydroxide.—The foregoing observations become of importance in view of the recent measurements of Jellinek and Gordon (*loc. cit.*) of the solubility product of cupric hydroxide.

* Here and elsewhere in this paper, the term "amorphous precipitate" is used to denote the non-gelatinous, apparently amorphous precipitates obtained when alkali hydroxide is added slowly to dilute solutions of cupric salts. They are sharply distinguished from the gelatinous precipitates produced by rapid mixing.

They precipitated their copper hydroxide from copper sulphate solution with an insufficiency of sodium hydroxide—exactly the condition for obtaining basic copper sulphate! The washed precipitate was suspended in alkali solution, and the copper-ion concentration was measured by means of a copper electrode. Their values for $[Cu^{\cdot\cdot}][OH']^2$ at 20° varied from $0{\cdot}7 \times 10^{-13}$ to $3{\cdot}0 \times 10^{-13}$, the mean being $1{\cdot}7 \times 10^{-13}$, but they could not confirm this by measurements with copper oxide. It is interesting to compare these values with those obtained from the curves (Fig. 1), assuming for the moment that the observed *E.M.F.*'s gave a true measure of the copper-ion concentration and that the basic precipitates had been completely decomposed by the excess of alkali. The hydroxyl-ion concentration when 40 c.c. of 0·0932*N*-sodium hydroxide had been added, the ionisation of the alkali being assumed to be complete, was $10^{-1{\cdot}91}$, and the cupric-ion concentration was $10^{-9{\cdot}55}$ (curve 1; *E.M.F.* = 0·217 volt), $10^{-8{\cdot}62}$ (curve 2; *E.M.F.* = 0·190 volt), and $10^{-7{\cdot}59}$ (curve 3; *E.M.F.* = 0·160 volt). Therefore $[Cu^{\cdot\cdot}][OH']^2$ is 4×10^{-14} (curve 1), $3{\cdot}6 \times 10^{-13}$ (curve 2), and $3{\cdot}9 \times 10^{-12}$ (curve 3). Although these values are meaningless, they are of the same order as those of Jellinek and Gordon. The precipitation of basic copper sulphate does not begin until p_H 5·6 has been attained, and from the method described by the author (*loc. cit.*), the presence of the sulphate in the precipitate being assumed not to affect greatly the precipitation p_H, it follows that the solubility product of cupric hydroxide is probably of the order 10^{-20}.*

Jellinek and Gordon do not refer to the work of Immerwahr (*Z. anorg. Chem.*, 1900, **24**, 269) on the potentials of copper electrodes in baryta solutions containing colloidal copper hydroxide or ignited copper oxide. The *E.M.F.*'s were so irregular that she did not calculate the solubility product of cupric hydroxide. Calculation shows that the solubility product varies from 3×10^{-12} to 8×10^{-16} for the colloidal hydroxide and to 8×10^{-23} for the ignited oxide. Allmand (J., 1909, **95**, 2151) traced the erratic behaviour of the copper electrode to the reaction $Cu^{\cdot\cdot} + Cu \rightleftharpoons 2Cu^{\cdot}$ taking place at the electrode, cuprous hydroxide being formed, and arrived by an indirect method at the value 10^{-19} for the solubility product of cupric hydroxide, which is of the same order as that calculated from the precipitation p_H, *viz.*, 10^{-20}. Jellinek and Gordon, who stated that to their knowledge no value for the solubility

* For the titration given in this vol., p. 2151, the limiting $[Cu^{\cdot\cdot}]$ was equivalent to 0·6 c.c. of *N*/10-sodium hydroxide in 120 c.c. Therefore $[Cu^{\cdot\cdot}] = 0{\cdot}3/120M/10 = 10^{-3{\cdot}6}$. $[OH'] = 10^{-14+5{\cdot}6} = 10^{-8{\cdot}4}$. Whence $[Cu^{\cdot\cdot}][OH']^2 = 10^{-20}$.

product of cupric hydroxide is recorded in the literature, had evidently not seen Allmand's paper.

This reducing action of the copper electrode accounts for its irreversible behaviour in the titrations, and the exceptionally low voltages obtained in No. 3 show that the reduction process was being considerably influenced by the nature of the layer deposited on the electrode.

The System CuO–SO_3–H_2O *at* 25°.—The substances used in the investigation were selected for their capacity to enter rapidly into equilibrium, namely, the amorphous basic sulphate, free sulphuric acid, and copper sulphate solution. The stock basic sulphate was kept as reactive as possible by suspending it in water. For certain equilibria, wet hydrated copper oxide had to be used.

The amorphous basic sulphate was prepared by adding *N*/10-sodium hydroxide (about 1·2 mols. for each mol. of copper sulphate) drop by drop and with continuous shaking to 10 litres of *M*/20-copper sulphate, every care being taken to prevent the formation of any gelatinous precipitate. The precipitate was washed by decantation with 20 to 30 litres of water, pressed on a Büchner funnel, and immediately immersed in water (Found in air-dried samples: CuO, 67·2, 67·6; SO_3, 17·1, 17·2. $4CuO,SO_3,4H_2O$ requires CuO, 67·7; SO_3, 17·0%). On keeping the precipitate, which was quite insoluble in water, in different quantities of sulphuric acid over-night, in every case 1·33 mols. of copper sulphate passed into solution for each molecule of sulphuric acid employed, thereby showing that the ratio of copper to sulphate in the residual solid remained unaltered, *viz.*, 4 : 1.

Quantities of the basic sulphate were placed in liquid phases (100 to 200 c.c.) composed of sulphuric acid and copper sulphate in various proportions, the quantities of acid being such that the rests should be small (about 2 g.). The mixtures were placed in a thermostat at 25° and shaken daily. Equilibrium was attained in less than a week, but 2 or 3 months were allowed to elapse before the final check analyses were made. The results shown in the most basic part of the isotherm necessitated the use of hydrated copper oxide. This was prepared by precipitation from a dilute copper sulphate solution at about 50° with a small excess of sodium hydroxide. It was somewhat dehydrated and brownish-black, but it had to be deposited at a moderately high temperature so that it should not be so gelatinous that it could not be washed free from alkali and sodium sulphate. This hydrated oxide was also used with sulphuric acid to confirm some determinations of the equilibria of mixtures prepared from the basic sulphate. The analyses of the various liquid phases and rests are in Table I.

TABLE I.

Liquid phases.		Rests.			
% CuO.	% SO_3.	% CuO.	% SO_3.	Mol. SO_3/ mol. CuO.	Solid phases.
0	0	84·45	6·17	0·073	CuO (hydrated) and $4CuO,SO_3,4H_2O$.
0	0	80·85	8·79	0·108	,, ,,
0	0	77·56	11·77	0·151	,, ,,
0	0	73·75	13·82	0·186	,, ,,
0	0	69·50	16·90	0·242	,, ,,
0	0	67·78	17·30	0·255	$4CuO,SO_3,4H_2O$.
0·02	0·02	67·90	17·60		,,
0·09	0·09	26·36	6·77		,,
0·12	0·12	9·24	2·43		,,
0·58	0·58	7·89	2·46		,,
3·17	3·19	31·23	9·85		,,
5·54	5·56	15·96	7·75		,,
7·17	7·18	24·10	10·27	0·314	,,
9·28	9·33	Eutectic			$4CuO,SO_3,4H_2O$ and $CuSO_4,5H_2O$.

The first six sets of data show that the addition of sulphuric acid to the hydrated copper oxide failed to cause any solution until the solid phase had assimilated sufficient sulphuric acid to convert it into the basic sulphate containing 4CuO to $1SO_3$. Neither copper nor sulphate could be found in the colourless liquid phases. The analyses given are those of the air-dried solid phases. These changed in colour as their sulphate content increased, passing from the brownish-black of the hydrated oxide through increasingly brighter shades of brown to greenish-brown and finally to the greenish-blue colour of the 4 : 1 salt. The basic sulphate did not change in colour on boiling, but decomposed on addition of varying quantities of alkali, yielding more basic products having similar colours. The other liquid phases were copper sulphate.

The results given in Table I are plotted in Fig. 2; the section BC has been constructed from the data of Bell and Taber (*loc. cit.*). The solid phase which was in equilibrium with the liquid phases represented by AB was $4CuO,SO_3,4H_2O$, for the tie-lines joining the points corresponding to each liquid phase and the point corresponding to its respective rest all pass through the point D, which indicates that the solid phase contained 67·7% CuO, 17·0% SO_3, and 15·3% H_2O (Schreinemakers). Had the solid phases in equilibrium with water as liquid phase been mixtures of two definite solid phases, it would have been expected that the points representing their compositions would lie on the straight line joining the two points corresponding to the compositions of the two solid phases. If in the present system the rests comprised mixtures of the basic salt $4CuO,SO_3,4H_2O$ and a definitely hydrated copper oxide, this line would have been one joining the point D to the

point, corresponding to the particular hydrated oxide, on the H_2O–CuO axis. Actually the points lie on one of two straight lines, DE and DF, where E represents $CuO,0{\cdot}28H_2O$ and F, $CuO,0{\cdot}05H_2O$. It appears from the phase rule that as the liquid phases which were in equilibrium with these highly basic rests were of fixed composition as far as could be ascertained, the rests were composed of two solid phases. Bearing in mind the gradual change in the colour of the rests, it seems probable that the two solid phases were the 4 : 1 sulphate and copper oxide, hydrated to varying extents. The degree of hydration of the copper oxide, although by no means fixed, was of the same order as that found in the ordinary precipitated black copper oxide, *i.e.*, corresponding approximately to $CuO,0{\cdot}25H_2O$. There appeared, however, a tendency for the hydration to become considerably less as the proportion of the 4 : 1 salt became predominant, shown by those points which fall on DF.

It follows from this work that at 25° there is only one basic sulphate of copper, *viz.*, $4CuO,SO_3,4H_2O$. Sabatier (*Compt. rend.*, 1897, **125**, 101) prepared it from copper oxide and copper sulphate solutions (not exceeding 1*M*). He stated that the salt was converted by saturated copper sulphate solution into a green salt, $5CuO,2SO_3,5H_2O$, treatment of which with water regenerated the 4 : 1 salt. This green salt was probably the ordinary 4 : 1 salt with copper sulphate adhering. In support of this view is the fact that the rest belonging to the liquid phase which contained 7·17% CuO (Table I) had, after filtration on a Büchner funnel, a composition corresponding approximately to the formula $3CuO,SO_3$, although, as its tie-line shows, the actual solid phase was the 4 : 1 salt.

Precipitation of Basic Cupric Chloride.—When *N*/10-sodium hydroxide or ammonia was added slowly with shaking to *M*/100-cupric chloride solutions, pale blue, amorphous precipitates were obtained, and the mother-liquors became alkaline to phenolphthalein, precipitation being complete, after the addition of 1·5 equivalents of alkali. If the additions were made quickly, precipitates did not separate until about 1 equivalent of alkali had been added, but the solutions became more and more colloidal and alkalinity occurred after the addition of 1·53 equivalents. When, however, more concentrated solutions were rapidly mixed, dark blue, gelatinous precipitates were obtained which, if the amount of alkali added did not exceed 1·5 equivalents, could be transformed by vigorous shaking with the mother-liquor into paler blue, amorphous forms. Provided that not more than 1·5 equivalents of alkali had been added during their formation, the amorphous precipitates did not

blacken on boiling; if a precipitate happened to be gelatinous, it darkened temporarily, but became pale blue and amorphous on continued boiling.

The System CuO–HCl–H_2O *at* 25°.—This system was investigated in exactly the same manner as the previous one. The substances used were moist hydrated copper oxide, moist basic cupric chloride, hydrochloric acid, and cupric chloride solution. On being washed by decantation, much of the basic chloride passed into pale blue, colloidal solution, and did not settle out after standing for a week. The colloidal solution was siphoned off and replaced by water, and the process was repeated, during a month, until the remaining precipitate was free from impurities. Samples which had been either air-dried or dried over fused calcium chloride agreed closely in composition with the formula $4CuO,2HCl,3H_2O$ (Found: CuO, 72·0; HCl, 16·5. Calc., CuO, 71·5; HCl, 16·4%). The salt was amorphous and insoluble in water; but after it had been boiled with water, the latter gave a faint opalescence with silver nitrate.

Equilibrium was attained in about a week, but the final analyses were not made until 3 months had elapsed.

The first four sets of data in Table II refer to solid phases which had been air-dried. The liquid phases were water. No copper chloride dissolved until each molecule of hydrated copper oxide had reacted with 0·5 equivalent of hydrochloric acid. Thereafter the solid phase was $4CuO,2HCl,3H_2O$, as shown by the point of intersection of the tie-lines in Fig. 3, and the liquid phases contained cupric chloride only.

TABLE II.

Liquid phases.		Rests.			
% CuO.	% HCl.	% CuO.	% HCl.	Mol. HCl/ mol. CuO.	Solid phases.
0	0	90·28	0·03	0·001	CuO (hydrated) and $4CuO,2HCl,3H_2O$.
0	0	79·30	11·49	0·315	" "
0	0	74·07	14·90	0·438	" "
0	0	72·47	16·57	0·499	$4CuO,2HCl,3H_2O$.
0·16	0·15	52·80	12·56	0·517	"
3·90	3·57	55·37	13·49		"
8·35	7·66	56·45	14·60		"
15·22	13·96	56·04	16·35		"
18·52	17·03	55·72	16·90		"
21·24	19·49	51·67	18·14		"
25·59	23·51				$4CuO,2HCl,3H_2O$ and $CuCl_2,2H_2O$.

The rests which had attained equilibrium with water, after being allowed to settle for a month, presented a striated appearance, pale green layers underlying layers of varying shades of dark

brown. The layers were roughly separated from one another by spraying with a very fine jet of water. The uppermost contained the least chloride, about 0·1 equivalent for each molecule of copper oxide, and the bottom pale green layers contained the most, about 0·3 equivalent. It was not possible to isolate the bottom layers quite free from the more basic, brown particles; probably the amount of chloride actually present in them was greater than 0·3 equivalent.

These observations seem to indicate that each of the highly basic rests was composed of a mixture of two solid phases as required

FIG. 2.

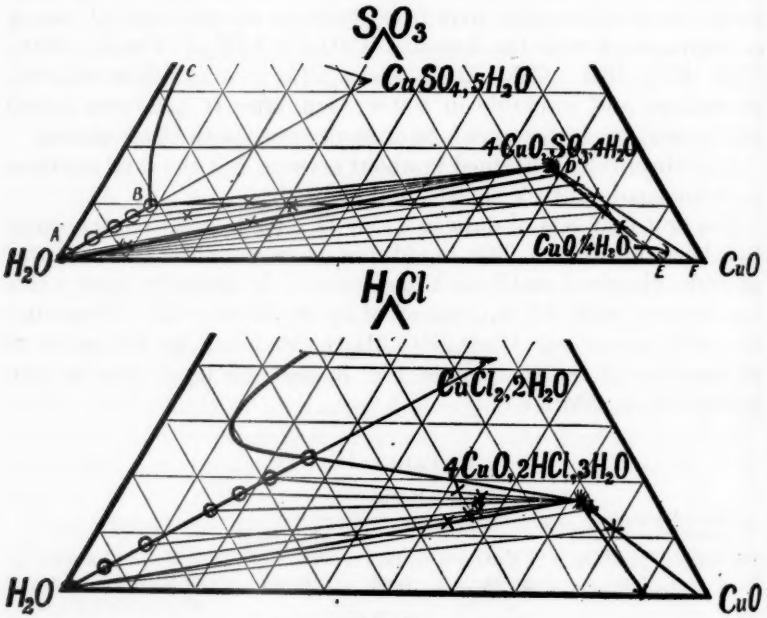


FIG. 3.

by the phase rule, and from Fig. 3 there appears to be no doubt that these were the definite basic chloride (greenish-blue) and dark brown copper oxide of varying hydration.

The basic chloride $4CuO,2HCl,3H_2O$ and the rests which contained more than 0·315 equivalent of chloride tended to pass into colloidal solution. Attempts were made to get some idea of the composition of the colloidal suspensions, and it was found that the basic chloride aggregates contained from 0·27 to 0·33 equivalent of chloride for each molecule of copper oxide.

The curve in Fig. 3 corresponding to those liquid phases which

exist in equilibrium with dihydrated cupric chloride was drawn from Foote's data (*J. Amer. Chem. Soc.*, 1923, **45**, 663).

Basic Cupric Nitrate.—Several basic nitrates have been described containing from 1·7 to 3 atoms of copper for each molecule of nitrate. The pale bluish-green precipitate formed when alkali, insufficient for complete reaction, is added to a dilute cupric nitrate solution has been shown by many workers to correspond to the formula $4CuO,2HNO_3,2H_2O$. The mineral gerhardtite has the same composition; in some specimens, however, the water content appears to be $1H_2O$.

When *N*/10-sodium hydroxide was carefully added to cupric nitrate solution, precipitation was complete and the solution became alkaline to phenolphthalein after the addition of 1·5 equivalents. The composition of the precipitate agreed with the above formula (Found: CuO, 66·8; HNO_3, 26·4. Calc., CuO, 66·3; HNO_3, 26·2%). The basic nitrate was insoluble in water, but on boiling with water it soon blackened and some passed into colloidal suspension. The salt was also much more readily decomposed by alkali than was either the sulphate or the chloride, so much so that when alkali was added rapidly to a cupric nitrate solution alkalinity was not produced until 1·9 equivalents had been added.

Basic Cupric Bromide.—The basic bromide produced by the oxidation of cuprous bromide and by the prolonged digestion of a solution of cupric bromide with copper oxide (Richards, *Chem. News*, 1891, **63**, 75; Sabatier, *Compt. rend.*, 1897, **125**, 103) has the formula $4CuO,2HBr,2H_2O$. The substance produced on gradual addition of alkali to cupric bromide solution has apparently not been examined. *N*/10-Sodium hydroxide gave a pale blue, amorphous precipitate and the mother-liquor became alkaline to phenolphthalein after approximately 1·5 equivalents had been added. This result suggests that the precipitate contained CuO and HBr in the molar ratio of 2 : 1. The (air-dried) precipitates formed by varying amounts of alkali, however, were slightly more basic [Found: (*a*) CuO, 60·55; HBr, 29·4. (*b*) CuO, 61·0; HBr, 30·3, corresponding respectively to $4CuO,1·91HBr,2·93H_2O$ and $4CuO,1·95HBr,2·52H_2O$]. It is fairly certain that they were essentially the 4 : 2 bromide, although the data are insufficient to state what was the exact water content. The basic bromide was insoluble in water and did not blacken when boiled with it. In common with the basic nitrate and the basic chloride, it had a marked tendency to pass into colloidal suspension when treated with water.

Discussion.

It has been shown that of the many basic sulphates and chlorides of copper which have been reported, only one definite sulphate and one definite chloride exist at 25°, *viz.*, $4CuO,H_2SO_4,3H_2O$ and $4CuO,2HCl,3H_2O$. Similar nitrate and bromide compounds have been shown to be produced by precipitation with alkali under similar conditions, *viz.*, $4CuO,2HNO_3,2H_2O$ and $4CuO,2HBr,2(?)H_2O$. They are similar not only in composition, but also in form, colour, and insolubility. All these salts are precipitated from solution at hydrion concentrations of about $10^{-5\cdot6}$. The similarity in their composition seems to be due to an intrinsic property of either the copper atom or the copper oxide molecule.

Previous workers have attempted to account for the sulphate and the nitrate as complex salts of ortho-acids, but such an explanation cannot be applied to the basic chloride or the basic bromide. The usual way of representing these basic salts as if they were double salts, *e.g.*, $CuSO_4,3Cu(OH)_2,H_2O$, is unsatisfactory, for they have none of the properties of double salts inasmuch as they are insoluble. Werner (*Ber.*, 1907, **40**, 4444), on the basis of his co-ordination theory, regards them as the normal salts of a hypothetical hexolcupric base, *e.g.*, $\left[Cu\left(\begin{matrix}HO\\HO\end{matrix}\!\!>\!Cu\right)_3\right]SO_4,H_2O$. This representation seems to be equally open to objection. Such a constitution would suggest that, contrary to the facts, the salt has to some extent the capacity of dissolving, which by comparison with difficultly soluble salts of metals, *e.g.*, lead and silver, is in some way connected with the nature of the acid radical, and would ionise in solution into "hexolcupric" and sulphate ions. The comparative inertness of these basic compounds to reaction and their similarity in properties to copper hydroxide seem to show that they are essentially compounds of this base of some unknown kind. Until something is known about their constitution it is perhaps better to represent them thus, $Cu_4(OH)_6SO_4,H_2O$. Were it known that the co-ordination number of bivalent copper is 6, the Werner theory might be considered to supply a tentative explanation why these basic salts contain copper and the acid in the equivalent ratio of 4 : 1. The ammine compounds of cupric salts have such widely varying compositions that no definite co-ordination number can be assigned. If the constitution of the cupric complexes in ammoniacal solutions be considered, the co-ordination number is probably 4.

Chatterji and Dhar state (Discussion on Colloids, *Faraday and Phys. Soc.*, 1920, 124) that the blackening on boiling of copper hydr-

oxide can be prevented by the addition of a little normal salt, which is adsorbed and thus renders the copper hydroxide stable. They do not appear to have considered what may be the effect of the formation of basic salts. The retention of the colour on boiling is a property of such salts—less marked, it is true, in the case of the nitrate (see pp. 2801, 2803, 2805).

Since the foregoing pages were written, Krüger has published some work on the basic sulphates of copper (*J. pr. Chem.*, 1924, **108**, 278). He obtained a product having the formula $4CuO,SO_3,4H_2O$, and also basic sulphates whose analyses, although irregular, indicated the formulæ $4CuO,SO_3,3{\cdot}5H_2O$, $4CuO,SO_3,5H_2O$, and $3CuO,SO_3,2{\cdot}5H_2O$. The water contents of the first two of these three substances are probably due to imperfect purification, and the last is undoubtedly a mixture of the definite basic salt and copper sulphate.

Summary.

(1) According to the manner of mixing and the quantity of alkali used, either apparently amorphous or gelatinous precipitates may be obtained by adding alkalis to solutions of the sulphate, chloride, bromide, or nitrate of copper.

(2) The individualities of the basic salts $Cu_4(OH)_6SO_4,H_2O$ and $Cu_4(OH)_6Cl_2,H_2O$ have been established.

(3) The behaviour of the $Cu|Cu(OH)_2,NaOH$ electrode has been shown to be erratic, and the value of Jellinek and Gordon for $[Cu^{\cdot\cdot}][OH']^2$ untrustworthy.

(4) Observations have been made on the darkening of suspensions of basic copper salts on boiling.

(5) The constitutions of the basic salts have been discussed with special reference to Werner's co-ordination theory.

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CCCLXXXVII.—*The Relationship between the Optical Rotatory Powers and the Relative Configurations of Optically Active Compounds. Part II. The Relative Configurations of the Optically Active Mandelic Acids and β-Phenyl-lactic Acids.*

By GEORGE WILLIAM CLOUGH.

IN Part I * (J., 1918, **113**, 526) it was shown that the formation of similar derivatives from the configuratively related compounds, *l*-lactic acid, *l*-glyceric acid, *d*-malic acid, and *d*-tartaric acid, was usually accompanied by changes of the same character in their optical rotatory powers. It was therefore assumed that, as a rule, the introduction of the same substituent into similarly constituted, optically active compounds possessing the same relative configurations produced alterations of the same character in their optical rotatory powers. The somewhat vague term "similarly constituted compounds" was used in this connexion, since it was not (and still is not) possible to state precisely the extent of the applicability of the rule. It applies to the members of such homologous series of optically active compounds as the aliphatic normal secondary alcohols and the simple α-hydroxy-acids. Indeed, the higher members of a homologous series being derivatives from the lower members, the rule would indicate that the optical rotatory powers of those optically active members of a series which are configuratively related would lie approximately on a curve. But not only do regularities occur in the optical rotatory powers of members of homologous series, they are evident (with few exceptions) in those of corresponding derivatives from the optically active mono- and di-hydroxy-propionic and -succinic acids.

The application of the principle to *d*-α-hydroxybutyric acid left no doubt that this compound possessed the same configuration as *l*-lactic acid, but the same confidence could not be felt in the conclusions which were drawn from the optical rotatory powers of compounds in which a phenyl or benzyl group was attached to the asymmetric carbon atom. In an endeavour to fix definitely the

* Errata in Part I: Page 532, line 5 from bottom, *for* "X=Bz, Y=Me" *read* "X=Bz, Y=Et."

Page 532, last line, *for* "−123·6" *read* "−247."

Page 540, line 3, *for* "+50·6°" *read* "−50·6°."

Since this paper was submitted for publication, the author's attention has been directed to a paper by Freudenberg and Markert entitled "Die Konfiguration der Mandelsaure" (*Ber.*, 1925, **58**, 1753). These authors have employed the method indicated in Part I and have confirmed the suggestion made therein concerning the configurations of the optically active mandelic acids.

configurations of the optically active forms of mandelic and β-phenyl-lactic acids, the optical rotatory powers of these compounds and some of their derivatives are considered in the present communication. The measurement by Freudenberg, Brauns, and Siegel (*Ber.*, 1923, **56**, 199) of the specific rotation of the amide of *l*-hexahydromandelic acid (prepared from *l*-mandelic acid) enabled those workers to confirm the suggestion that *l*-mandelic acid is a "*d*"-α-hydroxy-acid (Part I, p. 534). (For compounds containing one asymmetric carbon atom it appears to the present author desirable to retain the prefixes *d*- and *l*- with their conventional significance, but to denote their relative configurations by the prefixes "*d*"- and "*l*"-; *loc. cit.*, p. 534.) The optical rotatory powers of other derivatives from *l*-hexahydromandelic acid and from *l*-mandelic acid definitely indicate that these acids belong to the "*d*"- series of α-hydroxy-acids. This result is of importance in that it enables us to determine the configurations of *l*-benzoin, the related optically active glycols and of amygdalin with reference to that of *d*-tartaric acid. The experimental data quoted in tables I—V are also, in the author's opinion, sufficient to justify the allocation of *d*-β-phenyl-lactic acid to the "*d*"- series of α-hydroxy-acids. If this conclusion is accepted, it is possible to assign configurations to the glycols derived from this acid and also to the four optically active phenylglyceric acids (provided the assumption is made that *cis*-addition of hydroxyl occurs on oxidation of the cinnamic acids; compare Berner and Riiber, *Ber.*, 1921, **54**, 1945).

The molecular rotations of the standard "*d*"- acids in aqueous solution are lower * than those of the corresponding sodium (potassium or ammonium) salts (Table I). The same regularity is observed in the molecular rotations of *l*-hexahydromandelic acid, *l*-mandelic acid, *d*-β-phenyl-lactic acid and their salts.

The molecular rotations of the lower esters of the same acids increase as the molecular weights of the esters increase (Table II). The measurements by Wood and his collaborators of the optical rotatory powers and the optical dispersive powers of the optically active alkyl lactates and hexahydromandelates at various temperatures are especially valuable in connexion with the subject of this investigation.

The molecular rotations of the amides of the same acids compared with those of the methyl esters further illustrate the relation of

* Throughout this paper an "increase" of rotation denotes an increase in the numerical value of a dextrorotation or a decrease in the numerical value of a lævorotation. For the sake of clearness, the tabulated values are given for the "*d*"-forms, although in some cases the measurements were actually made on the enantiomorphous forms.

l-mandelic acid and of *d*-β-phenyl-lactic acid to the standard "*d*"-α-hydroxy-acids (Table III).

TABLE I.

The Molecular Rotations ($[M]_D$) *of Some Optically Active α-Hydroxy-acids in Aqueous Solution.*

	Acid.	Sodium salt.	Potassium salt.	References.
l-Lactic acid.	−2° ($c = 5$)	+ 13·2°	+13·7°	Purdie and Walker, J., 1895, **67**, 630.
l-Glyceric acid.	−2·3 ($c = 20$)	+ 20·6	+23·7	Frankland and Appleyard, J., 1893, **63**, 311.
d-Malic acid.	+3·0 ($c = 5$)	+ 16·2	+15·5	Stubbs, J., 1911, **99**, 2268.
d-Tartaric acid.	+21·3 ($c = 5$)	+ 59·9	+64·4	Landolt, *Ber.*, 1873, **6**, 1073.
l-Hexahydromandelic acid.	−21·3 (in alcohol)	+ 13·6	+ (ammonium)	Wood and Comley, J., 1924, **125**, 2639.
l-Mandelic acid.	−240 ($c = 1·6$)	−179	—	
d-β-Phenyl-lactic acid.	+38·0 ($c = 2·7$)	+ 79·5	+75·7	Clough.

TABLE II.

The Molecular Rotations of the Lower Esters of Some α-Hydroxy-acids.

		Methyl.	Ethyl.	*n*-Propyl.	*n*-Butyl.
l-Lactates.*	$[M]_D^{15°}$	+ 8·6°	+ 13·4°	+17·4°	+19·6°
l-Glycerates.†	$[M]_D^{15°}$	+ 5·8	+ 12·3	+19·1	+21·4
d-Malates.†	$[M]_D^{20°}$	+ 11·1	+ 19·3	+25·3	+26·4
d-Tartrates.†	$[M]_D^{20°}$	+ 3·7	+ 15·9	+29·7	+27·0
l-Hexahydromandelates.‡	$[M]_D^{30°}$	− 36·8	− 24·4	−15·5	−15·4
l-Mandelates.	$[M]_D^{20°}$	−276	−233	—	−209 (*iso*-)
d-β-Phenyl-lactates.§	$[M]_D^{20°}$	+ 8·5	+ 14·7 (at 17°)	—	—

* Wood, Such, and Scarf, J., 1923, **125**, 601. † For references, see Frankland and Gebhard, J., 1905, **87**, 865. ‡ Wood and Comley, *loc. cit.* § Clough; McKenzie and Barrow, J., 1911, **99**, 1021.

TABLE III.

The Molecular Rotations of the Amides of Some α-Hydroxy-acids.

	Methyl ester.	Amide.*
l-Lactic acid.	+ 8·6°	+ 19·6° (in water)
l-Glyceric acid	+ 5·8	+ 66·2 (in methyl alcohol)
d-Malic acid.	+ 11·1	+ 52·8 (in water)
d-Tartaric acid.	+ 3·7	+164 (in water)
l-Hexahydromandelic acid.	− 36·8 (at 30°)	+ 65·4 (in aqueous alcohol)
l-Mandelic acid.	−276	−144 (in water)
d-β-Phenyl-lactic acid.	+ 8·5	+104·2 (in ethyl alcohol) †

* For references, see Freudenberg, Brauns, and Siegel, *Ber.*, 1923, **56**, 195.
† McKenzie, Martin, and Rule, J., 1914, **105**, 1599.

From Table IV it is evident that acetylation of the methyl esters of the standard "*d*"-acids (except that of *d*-tartaric acid) causes the molecular rotations to increase. The introduction of one acetyl group into methyl *d*-tartrate raises the molecular rotation, but two acetyl groups in the molecule produce a depression in the molecular rotation. Acetylation of methyl *d*-β-phenyl-lactate is accompanied by an increase in the molecular rotation, but although methyl *l*-acetylmandelate possesses a higher specific rotation (− 146°) than methyl *l*-mandelate (− 166°), the molecular rotation of the former is lower than that of the latter compound. The molecular rotations of the benzoyl derivatives exhibit more irregularities; thus, the complete benzoylation of methyl *l*-lactate, of methyl *l*-glycerate, or of methyl *d*-tartrate produces decreases in the molecular rotations, but the introduction of one benzoyl group only into ethyl *d*-tartrate and the benzoylation of methyl *d*-malate are accompanied by increases in the molecular rotations. The values in Table IV show that an increase in the molecular (or the specific) rotation of methyl *d*-β-phenyl-lactate is produced on benzoylation and that an increase in specific rotation (but a decrease in molecular rotation) accompanies benzoylation of methyl *l*-mandelate. Whilst the data for the benzoyl derivatives do not confirm or refute the conclusions drawn respecting the relative configurations of *l*-mandelic and *d*-β-phenyl-lactic acids, the optical rotatory power of methyl *l*-phenylmethoxyacetate is in accordance with the view that *l*-mandelic acid is a "*d*"-α-hydroxy-acid.

TABLE IV.

The Molecular Rotations of the Acetyl, Benzoyl and Methyl Derivatives of Some α-Hydroxy-acids.

	Acetyl.	Benzoyl.	Methyl.
Methyl *l*-lactate (+8·6°).	+ 76·4°	− 35·6° *	+112·7°
Methyl *l*-glycerate (+5·8).	+ 24·6	− 87·5	+103·8
Methyl *d*-malate (+11·1).	+ 46·8	+ 15·0	+ 92·4
Methyl *d*-tartrate (+3·7).	+ 16·6 (mono-, in water)†	−280 (di-, at 100°)	+180·0
	− 39·6 (di-, in alcohol)		
Methyl *l*-mandelate (−276).	−304	−382 ‡	−173 (in acetone) §
Methyl *d*-β-phenyl-lactate (+8·5).	+ 16·3	+ 92·2 ‡	—

* Freudenberg and Rhino, *Ber.*, 1924, **57**, 1556. † Freudenberg and Brauns, *Ber.*, 1922, **55**, 1349. ‡ Clough. § McKenzie and Wren, J., 1910, **97**, 484.

It is worthy of note that the effect of a rise of temperature on the optical rotatory powers of the esters of *l*-hexahydromandelic acid (Wood and Comley, *loc. cit.*) is similar to that on the esters of *l*-lactic acid, *l*-glyceric acid, *d*-malic acid, *d*-tartaric acid, and

l-mandelic acid. The influence of organic solvents on optical rotatory power will be discussed by the author in a later paper.

The regularities observed in the influence of sodium, barium, and other halides on the optical rotatory powers of α-hydroxy-acids or their esters in solution have also been employed for determining the relative configurations of these optically active compounds. The data in Table V fully confirm the results already obtained. It should be pointed out that other inorganic compounds added to aqueous solutions of the acids in question do not always produce similar alterations in the rotatory powers. For example, boric acid produces a diminution in the optical rotatory power of *l*-("*d*"-)lactic acid (Henderson and Prentice, J., 1902, **81**, 658), but causes an elevation of that of *d*-tartaric acid (Biot).

TABLE V.

The Influence of Sodium Bromide on the Optical Rotatory Powers of Some Esters of α-Hydroxy-acids in Methyl-alcoholic Solution.

	In methyl alcohol.	In methyl-alcoholic sodium bromide (*N*).
Methyl *d*-malate.	+ 8·7° (*c* = 5)	− 8·0° (*c* = 5)
Ethyl *d*-malate.	+ 11·6 (*c* = 5)	− 2·4 (*c* = 5)
Methyl *d*-tartrate.	+ 4·6 (*c* = 5)	− 8·4 (*c* = 5)
n-Propyl *d*-tartrate.	+ 16·0 (*c* = 5)	+ 2·6 (*c* = 5)
Methyl *l*-mandelate.	−142 (*c* = 3)	−172 (*c* = 3)
Ethyl *l*-mandelate.	−117 (*c* = 10)	−150 (*c* = 10)
Methyl *d*-β-phenyl-lactate.	− 2·4 (*c* = 2·7)	− 16·3 (*c* = 2·7)
Ethyl *d*-β-phenyl-lactate.	+ 0·8 (*c* = 5)	− 12·0 (*c* = 5)

That the principle employed in this investigation also leads to correct deductions in other classes of compounds is shown by Karrer's confirmation of the present author's view that *l*-asparagine, *l*-aspartic acid, and *l*-leucine are configuratively related to *d*-("*l*"-) alanine (*Helv. Chim. Acta*, 1923, **6**, 957; see Part I, p. 539). Moreover, a study of the optical rotatory dispersive powers of a number of corresponding derivatives from the optically active α-amino- and α-hydroxy-propionic acids has revealed regularities from which Freudenberg and Rhino have drawn the conclusion that *l*-("*d*"-) alanine possesses the same configuration as *l*-("*d*"-)lactic acid (*Ber.*, 1924, **57**, 1551; see Part I, p. 548).

EXPERIMENTAL.

l-*Mandelic Acid*.—In water (*c* = 1·59): $\alpha^{14°}_{5893}$ (*l* = 2) − 5·03°, $\alpha^{14°}_{5780}$ − 5·28°, $\alpha^{14°}_{5461}$ − 5·98°, $\alpha^{14°}_{4078}$ − 13·55°; $[\alpha]^{14°}_{5893}$ − 158°, $[\alpha]^{14°}_{5780}$ − 166°, $[\alpha]^{14°}_{5461}$ − 188°, $[\alpha]^{14°}_{4078}$ − 426°.

In aqueous sodium chloride (4*N*) (*c* = 1·59): $\alpha^{14°}_{5461}$ (*l* = 2) − 6·45°; $[\alpha]^{14°}_{5}$ − 203°.

Ethyl l-*Mandelate*.—$d^{15°}_{4°}$ 1·128; $\alpha^{15°}_{5893}$ (*l* = 0·5) − 73·04°, $\alpha^{15°}_{5780}$ − 76·55°, $\alpha^{15°}_{546}$ − 88·10°; $[\alpha]^{15°}_{5893}$ − 129·4°, $[\alpha]^{15°}_{5780}$ − 135·7°, $[\alpha]^{15°}_{5461}$ − 156·4°.

In methyl alcohol ($c = 10$): $\alpha^{15°}_{5893}$ ($l = 2$) $-$ 23·48°, $\alpha^{15°}_{5780}$ $-$ 24·38°, $\alpha^{15°}_{5461}$ $-$ 28·20°, $\alpha^{15°}_{4073}$ $-$ 65·0°; $[\alpha]^{15°}_{5893}$ $-$ 117·4°, $[\alpha]^{15°}_{5780}$ $-$ 121·9°, $[\alpha]^{15°}_{5461}$ $-$ 141·0°, $[\alpha]^{15°}_{4078}$ $-$ 325°.

In methyl-alcoholic sodium bromide (N) ($c = 10{\cdot}12$): $\alpha^{15°}_{5893}$ ($l = 2$) $-$ 30·30°, $\alpha^{15°}_{5461}$ $-$ 36·55°; $[\alpha]^{15°}_{5893}$ $-$ 149·6°, $[\alpha]^{15°}_{5461}$ $-$ 180·5°.

Methyl l-*phenylbenzoyloxyacetate*, prepared by the action of benzoyl chloride on methyl *l*-mandelate in presence of pyridine, boiled at 224—225°/18 mm.

$d^{20°}_{4°}$ 1·217; $\alpha^{20°}_{D}$ ($l = 0{\cdot}5$) $-$ 86·05°; $[\alpha]^{20°}_{D}$ $-$ 141·4°.

Methyl l-β-*phenyl-lactate* was prepared by McKenzie and Martin's method (J., 1913, **103**, 117).

$d^{20°}_{4°}$ 1·129; $\alpha^{20°}_{D}$ ($l = 1$) $-$ 5·35°; $[\alpha]^{20°}_{D}$ $-$ 4·74°.

Methyl d-α-*acetoxy*-β-*phenylpropionate*, m. p. 30—31°, b. p. 185°/20 mm., was prepared by the action of acetyl chloride on methyl *d*-β-phenyl-lactate in presence of pyridine.

$d^{18°}_{4°}$ 1·125; $\alpha^{18°}_{D}$ ($l = 1$) $+$ 8·23°; $[\alpha]^{18°}_{D}$ $+$ 7·33°.

Methyl l-α-*benzoyloxy*-β-*phenylpropionate*, b. p. 224—225°/16 mm., was prepared by the action of benzoyl chloride on methyl *l*-β-phenyl-lactate in presence of pyridine.

$d^{20°}_{4°}$ 1·161; $\alpha^{20°}_{D}$ ($l = 1$) $-$ 37·65°; $[\alpha]^{20°}_{D}$ $-$ 32·45°.

The above esters required the correct amounts of sodium hydroxide for complete saponification, which was unaccompanied by change of sign of rotation. Some racemisation may have occurred in the preparation of methyl *l*-phenylbenzoyloxyacetate; Freudenberg and Markert (*loc. cit.*) give $[\alpha]^{20°}_{578}$ $-$ 159·9° for this compound.

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ROYAL VETERINARY COLLEGE,
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CCCLXXXVIII.—*The Action of Silica on Electrolytes. Part II.*

By ALFRED FRANCIS JOSEPH and HENRY BOWEN OAKLEY.

THE action of silica on two classes of electrolytes—acids * and salts—has already been studied (Joseph and Hancock, J., 1923, **123**, 2022). Its effect on bases is now described. It must again be

* The experiments with acids have been repeated with purified "silica gel" with the same result. There has been some correspondence in *Nature* (Jan. 31st, March 28th, and April 4th) on this subject, but the present authors have not yet obtained experimental evidence requiring a change of opinion.

emphasised that a high degree of purity of the silica is essential for work of this kind, as the presence of a small quantity of basic impurity has an important effect on its properties. For example, a sample of silica gel which retained 6% of water after drying at 180° retained only 3·2% if it had been washed with hydrochloric acid (followed by water) before being dried.

Silicates of the Alkali and the Alkaline-earth Metals.—Many studies on these substances at high temperatures have been carried out in recent years, but data as to reactions taking place in presence of much water at the ordinary temperature are scanty. The following facts bear on what follows: Potassium seems to form silicates of greater stability in water and lower solubility than sodium: the properties of potash glass bear this out, and also the fact (Morey, *J. Amer. Chem. Soc.*, 1914, **36**, 230) that the compound $KHSi_2O_5$ may be left for hours with water at 100° without undergoing appreciable decomposition. Calcium silicate is less soluble in water than the barium salt. The sodium silicates, even when containing a high proportion of silica, are all acted on by water to a noticeable degree.

The equilibrium between silicic acid and sodium hydroxide was studied by constructing a titration curve for a "water glass" solution containing 2 mols. of silica to 1 mol. of sodium oxide. The first points on the curve were obtained by the addition of hydrochloric acid, and the later ones by the addition of sodium hydroxide. In each case the hydroxyl-ion concentration was determined by p_H measurement, and the amount of sodium silicate present was found by subtracting the quantities of hydrochloric acid and hydroxyl from the total sodium. The results are in Table I. If the sodium oxide neutralised is plotted against p_H, the curve shows a definite inflexion when the solution contains 2 mols. of neutralised sodium oxide to 1 mol. of silica. The p_H at which the ratio is half this is very nearly 10, and this corresponds to the value 10^{-10} for the first dissociation constant of silicic acid. The combination between the second molecule of sodium oxide takes place between p_H values of 11·6 and 12·6, indicating that the second dissociation constant of the acid is about 10^{-12}. The curve is typical of the combination of a strong base with a weak dibasic acid.

TABLE I.

Solution contains 0·0186 mol. of silica per litre.

p_H	3·2	9·40	9·90	10·0 *	10·72
Mols. Na_2O neutralised	0·0	0·0017	0·0043	0·0046 *	0·0086
p_H	11·77	12·28	12·31	12·53	12·63
Mols. Na_2O neutralised	0·0112	0·0180	0·0278	0·0745	0·1570

The point marked * was obtained by interpolation.

The Action of Alkaline Hydroxides on Silica.—When pure silica is acted on by an alkaline hydroxide, neutralisation of the base commences immediately, and the extent to which the reaction proceeds is dependent on the nature and the concentration of the base, the quantity of silica (at the surface of which the reaction takes place), as well as on the usual factors such as time of contact and temperature. The fineness of the silica will of course determine the amount of reactive surface, so that different specimens will not necessarily give the same quantitative results, although different series will be comparable amongst themselves.

The immediate effect is the production of a silicate at the surface of the silica. This is followed by its partial dissolution caused by the solvent and hydrolytic action of the water. After a time, equilibrium is approached between the silicate in the solid and that in the liquid phase. Increase of concentration of either of the reagents causes an increase in the amount of silicate in each phase.

For equal concentrations of different bases, the amount of solid silicate formed depends on the solubility relationships of the silicate of the base used, being great where the solubility is small (as in the case of calcium) and small where the solubility is large (as in the case of sodium).

These statements are illustrated by the results tabulated below. The amount of silica taken is given as g. per 100 c.c. : in all other cases, concentrations are expressed as g.-equiv. per litre.

The silica was purified, and the p_H measurements were made, as previously described. The reactions were carried out in wax-coated glass flasks. The amount of hydroxyl-ion remaining in solution was calculated from the p_H measurements by means of the values of Michaelis for $1/\log K_w$ at the temperatures at which the experiments were made: these varied between 33° and 38°. From the hydroxyl-ion concentration, the concentration of free base was calculated from its known degree of dissociation at the working concentration.

Titration with standard hydrochloric acid gave the concentration in solution of the free base plus soluble silicate, and this, subtracted from the amount of base taken, gave the amount of the base retained in the solid phase. Neither thermostats nor shakers were used in this work.

TABLE II.

Effect of time on the progress of the reaction.

Silica 0·5%. Base 0·0365*N*.

Time	20 hours	48 hours	70 hours	12 days
% NaOH neutralised	53	63	86	94
% $Ca(OH)_2$ neutralised	68	79	98	99

TABLE III.

Comparison of the amounts of solid silicate formed from different bases after 1 day. Initial concentration of base 0·405*N*.

Base.	Base neut.	Fraction of base neutr.	Solid silicate per litre.	Silicate in soln.	Solid as % of total.
NaOH	0·027	0·66	0·0014	0·026	5·2
KOH	0·029	0·71	0·0019	0·027	6·5
$Ba(OH)_2$	0·021	0·54	0·0063	0·014	30
$Ca(OH)_2$	0·034	0·84	0·034	0·000	100

The results follow the solubility relationships of the silicates of these four bases.

The barium experiment was made at a different time, and the initial concentration of the base was 0·0392.

TABLE IV.

Effect of the concentration of the base on the amounts of silicate formed in the solid and liquid phases after 2 days.

Initial NaOH.	Final NaOH.	Total silicate.	Solid silicate.	Silicate in soln.
0·004	0·00016	0·0038	Small	0·0038
0·014	0·00058	0·0134	0·00024	0·0132
0·030	0·00159	0·0285	0·00032	0·0282
0·060	0·00828	0·0515	0·00112	0·0504

TABLE V.

Effect of the amount of silica taken on that of the silicates formed in the solid and liquid phases after 8 days.

Base.	NaOH, 0·040*N*.		KOH, 0·040*N*.			$Ba(OH)_2$, 0·039*N*.		$Ca(OH)_2$, 0·038*N*.	
% Silica taken.	0·5	1·0	0·5	1·0	2·0	0·5	1·0	0·5	1·0
Solid silicate	0·0014	0·0027	0·0011	0·0021	0·0047	0·0063	0·0138	0·0349	0·0351
Silicate in soln.	0·0366	0·0369	0·0379	0·0383	0·0358	0·0054	0·0092	0·0028	0·0027
% Base neutr.	94	97	97	100	100	30	58	99	99

(*Note.*—The experiments with sodium hydroxide were carried out with a different specimen of silica : this does not affect the relationships which the above table is designed to show.)

From the above two tables it appears that there is (*a*) a direct equilibrium between solid silica, solid silicate and liquid phase (hydroxide and silicate in solution) which is the main factor in the case of sodium and potassium; and (*b*) an ordinary solubility relationship between solid and soluble silicates which is the main factor where, as in the case of calcium and barium, no easily soluble silicates exist. It follows from (*a*) that any reduction in the

amount of free silica should be accompanied by a reduction in the amount of solid silicate, and this is shown by the following figures for the time effect of a stronger solution of sodium hydroxide on silica: the gradual passage into solution of the silica is accompanied by a fall in the amount of solid silicate.

TABLE VI.

Simultaneous disappearance into solution of silica and solid silicate. 1% Silica = 0·167 mol. per litre. NaOH, 0·0101*N*.

Time.	p_H.	Total silicate.	Solid silicate per litre.
5 hours	11·94	0·0768	0·0057
1 day	11·41	0·0937	0·0046
2 days	11·15	0·0972	0·0040
4 „	11·00	0·0981	0·0039
8 „	10·93	0·0986	0·0037

Effect of Neutral Salts on the Reaction.—The reactions between neutral salts and silica have been dealt with in the previous paper: acidity is always developed and some of the base goes into the solid phase. The addition of a salt to a mixture of silica and alkali should favour the formation of insoluble silicate by depressing the solvent and hydrolytic action of the water, and this is found to be the case. Table VII gives the results of parallel experiments carried out with and without the addition of the chloride of the base concerned.

TABLE VII.

1% Silica and 0·04*N*-base. Time of standing, 1 day. Conc. of salt soln. = *N*.

Fraction of added base found in solid phase.

Base.	Without salt.	With salt.
NaOH	0·030	0·078
KOH	0·035	0·149
$Ca(OH)_2$	0·70	0·85
$Ba(OH)_2$	0·161	0·210

Experiments carried out with sodium chloride and different amounts of silica showed that, as before, the amount of silica determined that of the solid silicate formed (which is, of course, very small in the absence of free base). Titration methods could not be applied, but the hydrogen ions liberated were equivalent to the solid silicate, and this is seen to be roughly proportional to the silica taken.

TABLE VIII

Silica taken.	p_H of mixture.	H-ion conc.
1%	4·01	0·00010
2%	3·74	0·00018

Summary.

(*a*) The action of an alkaline hydroxide on silica results in the formation of a solid silicate, part of which passes into solution. The amount of solid silicate formed is very small with sodium and potassium, about 50% in the case of barium, and nearly 100% with calcium. These results are in accordance with the solubilities of the silicates of these bases.

(*b*) In the case of sodium and potassium, the small amount of solid silicate produced is roughly proportional to the weight of silica taken, although the amount of silicate in solution is only slightly affected. These relationships show that the solid phases (silica and silicate) are directly concerned in the equilibrium.

(*c*) The addition of a neutral salt increases considerably the amount of solid silicate produced.

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CCCLXXXIX.—*Isomeric Change in Aromatic Compounds. Part I. The Conversion of Diacylanilides into Acylamino-ketones.*

By ARTHUR WILLIAM CHAPMAN.

IN the course of an investigation on imino-aryl ethers it was found that when a current of dry hydrogen chloride was passed through fused dibenzanilide at 250—270° benzoyl chloride and benzanilide were produced:

$$PhN(COPh)_2 + HCl = PhNH{\cdot}COPh + PhCOCl.$$

Diacetanilide decomposed in a similar manner, yielding at 150—170° acetyl chloride and acetanilide.

Diacylanilides, when heated in presence of either hydrogen chloride or zinc chloride, are converted into the corresponding acylamino-ketones by what has been regarded as an intramolecular change (Chattaway and Lewis, J., 1904, **85**, 386, 589, 1663; Angel, J., 1912, **101**, 515; Derick and Bornmann, *J. Amer. Chem. Soc.*, 1913, **35**, 1269). Migration does not occur in the absence of a catalyst of this kind, and the necessary conditions are exactly those under which hydrogen chloride decomposes the diacylanilides. It seems, then, more reasonable to suppose that, with hydrogen chloride as catalyst, the change takes place by decomposition of the diacylanilide into acyl chloride and anilide and recondensation to yield the ketone and hydrogen chloride:

$$C_6H_5{\cdot}NAc_2 + HCl \rightarrow C_6H_5{\cdot}NHAc + AcCl \rightarrow C_6H_4Ac{\cdot}NHAc + HCl.$$

Zinc chloride, especially if it has been allowed to become damp, usually contains a little free hydrogen chloride, and this would account for its catalytic activity. Diacetanilide remained almost unchanged when heated at 140—160° in presence of dry zinc chloride alone, but was readily converted into *p*-acetylaminoacetophenone when hydrogen chloride was passed into the mixture. The hydrogen chloride therefore appeared to be the essential factor, although the zinc chloride no doubt assisted by acting as a condensing agent in the second stage of the conversion.

The conversion of diacylanilides into acylamino-ketones furnishes yet another example of the numerous isomeric changes in the aromatic series which have been shown to proceed by fission of the mobile group followed by recondensation, such as the Hofmann–Martius change (Beckmann and Correns, *Ber.*, 1922, **55**, 852), the Fischer–Hepp change (O. Fischer, *Annalen*, 1895, **286**, 145), the conversion of phenolic esters into hydroxy-ketones (Skraup and Poller, *Ber.*, 1924, **57**, 2033), and the isomeric change of imino-aryl ether hydrochlorides (J., 1922, **121**, 1676; 1923, **123**, 1150).

It is proposed to extend the present study to other similar isomeric changes which have not yet been investigated from this point of view.

Experimental.

Decomposition of Dibenzanilide and of Diacetanilide by Hydrogen Chloride.—Dry hydrogen chloride was passed through the fused diacylanilide, the temperature of which was gradually raised until distillation began and was then maintained constant until no more liquid came over.

Diacetanilide (20 g.) yielded a colourless distillate (6·7 g.), b. p. 51—53°, which reacted with *p*-toluidine to give aceto-*p*-toluidide (m. p. 147°). The residue (11·5 g.), b. p. 286—290°, crystallised from benzene or water in shining leaves (m. p. 114°, alone or mixed with acetanilide).

p-Aminoacetophenone, *p*-acetylaminoacetophenone and acetanilide did not yield any acetyl chloride on treatment with hydrogen chloride even at 200—250°.

Dibenzanilide (10 g.) yielded benzoyl chloride (2·1 g.; b. p. 193—200°; converted by phenol and sodium hydroxide into phenyl benzoate, m. p. 68—69°) and benzanilide (4·8 g.; m. p. after recrystallisation 159—160°, not depressed by admixture with an authentic specimen).

Conversion of Diacetanilide into p-*Acetylaminoacetophenone.*—A mixture of diacetanilide (20 g.) and powdered dry zinc chloride (3 g.) was heated at 140—160° while hydrogen chloride was led into

it for 4½ hours. Since *p*-acetylaminoacetophenone is difficult to isolate as such, the product was hydrolysed by boiling with concentrated hydrochloric acid (150 c.c.) and the solution was made alkaline with solid sodium hydroxide, steam-distilled to remove aniline, cooled, and filtered. Boiling light petroleum extracted from the precipitate about 2 g. of *p*-aminoacetophenone (m. p. 106—107°, not depressed by admixture with an authentic sample).

In a similar experiment without hydrogen chloride, no *p*-aminoacetophenone was isolated from the light petroleum extract, but the alkaline aqueous liquor gave a deep red dye on diazotisation and coupling with β-naphthol. In two control experiments in which diacetanilide was heated alone, no *p*-aminoacetophenone could be detected even by the diazo-reaction.

p-Aminoacetophenone was also obtained by passing acetyl chloride vapour through fused acetanilide and zinc chloride, but was accompanied by much diphenylethenylamidine (m. p. 132—133°), formed by the condensation of 2 mols. of acetanilide with elimination of acetic acid.

THE UNIVERSITY, SHEFFIELD. [*Received, October 14th*, 1925.]

CCCXC.—*The Partial Pressures of Water Vapour and of Sulphuric Acid Vapour over Concentrated Solutions of Sulphuric Acid at High Temperatures.*

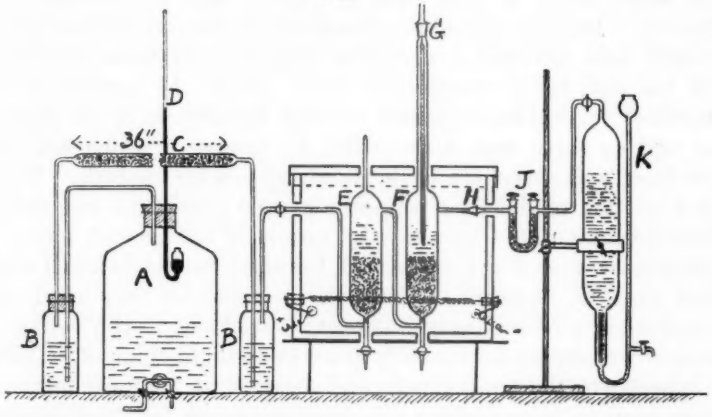
By JOHN SMEATH THOMAS and WILLIAM FRANCIS BARKER.

THIS investigation was undertaken with the object of extending the measurements of Thomas and Ramsay (J., 1923, **123**, 3256). These authors determined the partial pressures of the sulphuric acid only. It seemed desirable also to obtain data regarding the partial pressures of the water vapour in equilibrium with concentrated solutions of the acid over the same range of temperature.

At an early stage in the work it became evident that the results obtained in the previous investigation were uniformly low. Further examination revealed two sources of error: (*a*) adsorption of sulphuric acid vapour on the glass wool employed to remove "mist," and (*b*) the possibility that the liquid was not in thermal equilibrium with the heating bath. Of these, the former is the more serious; it had been foreseen, but the precautions taken against it now appear to have been inadequate. As regards the second possibility, in the previous work the actual temperature of the acid was not measured; it was assumed to have attained the temperature of the bath, considerable time having been allowed for this purpose.

In this investigation, the apparatus was modified to eliminate these errors as far as possible, and measurements of the partial pressures of the water vapour and of the sulphuric acid were made at a series of temperatures ranging from 180° to 300°. The dynamical method (*loc. cit.*) was again employed, the partial pressures being calculated from the experimental data by the method of Foote and Scholes (*J. Amer. Chem. Soc.*, 1911, **33**, 1309), but whereas in the previous work the volume of the water vapour removed by the current of air was either neglected, as in the case of the more concentrated solutions examined, or calculated * from Burt's measurements of the total vapour pressure (J., 1904, **90**, 1339), the sulphuric

FIG. 1.



acid partial pressures of these more dilute solutions being assumed to be negligible, in the present work it was obtained from the actual weight of water removed by the air. The partial pressure is then given by the formula

$$p = 760\ v/(v_1 - v_2),$$

in which v represents the volume of the water vapour or the sulphuric acid vapour as the case may be, v_1 the volume of air (reduced to N.T.P.), and v_2 the combined volumes of the water vapour and the sulphuric acid vapour removed during the experiment. In calculating these volumes the value 22·3 litres was taken for the gram-molecular volume.

EXPERIMENTAL.

The modifications in the apparatus can best be understood by reference to Fig. 1.

* In the previous communication reference to this correction for the volume of the water vapour was inadvertently omitted.

A current of air from the aspirator A was dried and freed from carbon dioxide by passing it through the vessels B and C, containing concentrated sulphuric acid and soda-lime, respectively. The aspirator was fitted with the manometer D in order that the air supply might be kept at constant pressure—a pressure equivalent to 900 mm. Hg was found to be convenient. This greatly facilitated the experimental manipulation of the apparatus. From C, the dried and purified air passed through the saturators E and F, which contained the acid solution under investigation.

These saturators, each having a working capacity of approximately 250 c.c., were constructed and arranged in the thermostat in the manner indicated in the diagram. They were half filled with short pieces of glass tube of narrow bore and worked very efficiently; the tiny air bubbles produced by the constricted vertical air inlet tube followed a circuitous path and remained in contact with the acid for a considerable time. From the bottoms of the saturators vertical tubes passed through the bottom of the thermostat and to these taps were sealed, by means of which acid was introduced and specimens could be withdrawn for analysis. To the upper portion of the final saturator a wide glass tube was sealed; a thermometer, fitted into this by means of the ground joint, G., dipped below the surface of the acid, the actual temperature of which could thus be observed. Although no regulator was used, this temperature remained very constant; variations in the voltage of the electrical supply occasionally gave rise to slight changes. During an experiment the temperature was observed at 2-minute intervals. These readings were plotted and from the graph the mean temperature was obtained.

The thermostat consisted of a double-walled box, the outer wall being of galvanised iron and the inner wall, which was separated from the outer by an air space of about ½ inch, of asbestos slate. Through each side of the box two insulated terminals passed, leading to the heating units—spirals of nichrome wire—any of which could be used or cut out at will, according to the temperature required. The final temperature regulation was effected by means of an adjustable external resistance.

The air, saturated with acid vapour, passed from the final saturator through the absorbing vessels, J, into the measuring device, K. Two of these vessels were employed, but only one is shown in the diagram. Each had a capacity of about 300 c.c.; the volume between the fixed marks had been carefully determined and the lower limb was graduated. During the experiment water was run out at such a rate as to keep the air under atmospheric pressure.

Each experiment involved two determinations: (*a*) the total

weight of vapour (sulphuric acid and water) removed by a given volume of air, and (*b*) the weight of the removed sulphuric acid vapour alone. For the determination of the total weight of vapour a series of absorption tubes was used. These contained solid sodium hydroxide followed by granular calcium chloride and were carefully weighed before and after each experiment with all the usual precautions. For the estimation of the sulphuric acid vapour the conductivity method described (*loc. cit.*) was employed, except in the case of the 99·23% solution; no water vapour could be detected in the vapour from this and the increase in weight of the absorption tubes was assumed to be entirely due to sulphuric acid.

Connexion between the absorbing vessels and the final saturator was made by means of the carefully ground joint, H, which was situated inside the thermostat, thus obviating the premature condensation of vapour. The inner portion of this joint projected into a small bulb, not shown in the diagram, the object of which was to prevent the creeping of acid along the surface of the glass into the absorbing vessels.

Preliminary experiments having disclosed that the use of glass wool for the prevention of the mechanical transference of acid in the form of "mist" leads to serious errors, this end was attained by using an extremely slow current of air; in the final experiments the rate of flow never exceeded 150 c.c. per hour. On examining the brightly illuminated space above the surface of the acid, no trace of mist could be seen.

The strength of the various acid solutions examined was determined gravimetrically. Analysis of four samples from each saturator at the close of the series of determinations revealed no change in concentration.

The Variation of the Partial Pressures with the Temperature.

Five series of measurements were made on sulphuric acid solutions of concentrations between 89·25 and 99·23% H_2SO_4, in each case at a number of different temperatures ranging from 180° to 295°; on account of the lower boiling points of the more dilute solutions measurements could not be made at the higher temperature. The results are in Table I, in which the pressures are expressed in mm. of mercury.

In calculating the values in columns 2, 3, and 4 the assumption has been made that the sulphuric acid vapour is not dissociated, whilst the values in the next three columns are based on the assumption that complete dissociation of the acid vapour occurs. The values for the dissociated acid cannot be obtained from the corresponding figures for undissociated acid by means of the expres-

TABLE I.

t.	$p_{H_2SO_4}$.	p_{H_2O}.	P.	Assuming complete dissociation. p'_{SO_3}.	p'_{H_2O}.	P'.
			Series A. 89·25% H_2SO_4.			
183·0°	0·5	78·8	79·3	0·5	79·2	79·7
197·5	1·3	116·9	118·2	1·3	118·0	119·3
216·5	2·1	233·1	235·2	2·1	234·6	236·7
230·0	3·6	306·3	309·9	3·6	308·4	312·0
241·5	5·3	414·8	420·1	5·3	417·2	422·5
			Series B. 91·26% H_2SO_4			
191·0	0·6	50·7	51·3	0·6	51·3	51·9
205·0	1·9	84·7	86·6	1·9	86·1	88·0
222·0	4·5	158·5	163·0	4·5	162·1	166·6
242·5	6·4	271·6	278·0	6·4	275·7	282·1
252·5	11·3	385·3	396·6	11·1	390·7	401·8
258·0	13·6	448·7	462·3	13·4	454·2	467·6
262·5	16·3	411·1	427·4	15·9	419·0	434·9
			Series C. 95·06% H_2SO_4.			
180·0	2·1	10·1	12·2	2·1	12·2	14·3
200·0	4·8	21·2	26·0	4·8	25·8	30·6
215·5	8·5	46·5	55·0	8·4	54·4	62·8
232·0	13·4	91·9	105·3	13·2	103·5	116·7
244·5	19·9	120·1	140·0	19·4	136·4	155·8
252·0	20·0	156·5	176·5	19·5	172·0	191·5
261·0	27·9	180·7	208·6	26·9	201·1	228·0
270·0	39·9	254·9	294·8	37·8	279·6	317·4
280·5	52·0	310·0	362·0	48·7	351·9	400·6
282·0	52·6	350·2	402·8	49·2	376·5	425·7
			Series D. 98·06% H_2SO_4.			
204·0	5·9	0·0	5·9	5·9	5·9	11·8
218·5	9·8	1·5	11·3	9·7	11·2	20·9
234·5	14·7	3·2	17·9	14·4	17·6	32·0
249·0	28·5	2·6	31·1	27·5	30·0	57·5
261·0	38·8	5·0	43·8	36·9	41·6	78·5
273·0	61·9	5·3	67·2	57·2	62·5	119·7
285·0	91·6	11·8	103·4	81·8	92·2	174·0
295·0	132·3	14·7	147·0	112·7	125·2	237·9
			Series E. 99·23% H_2SO_4.			
211·0	33·2	—	33·2	33·2	33·2	66·4
225·0	49·9	—	49·9	49·9	49·9	99·8
227·0	55·4	—	55·4	55·4	55·4	110·8
244·0	84·1	—	84·1	84·1	84·1	168·2
261·0	163·8	—	163·8	163·8	163·8	327·6
270·0	229·8	—	229·8	229·8	229·8	459·6
281·0	272·3	—	272·3	272·3	272·3	544·6
290·0	381·5	—	381·5	381·5	381·5	763·0

sions $p_{H_2SO_4} = p'_{SO_3}$ and $P'_{diss.} = 2p_{H_2SO_4} + p_{H_2O}$, where p' refers to acid in which dissociation is assumed. The reason for this lies in the method, which is applicable whichever assumption is made, but which does not allow of results being translated from one basis to the other because of the volume change which must be taken into account. The following example, taken from an actual experi-

ment on 91·26% H_2SO_4, makes this point clear. In this example the question is simplified because the volume of air used in the two runs chanced to be the same. 292·3 C.c. of air at *N.T.P.* were passed through the acid (262·5°). The increase in weight of the absorption tubes was 0·3554 g. and the weight of acid absorbed in conductivity water was 0·0630 g. *Assuming no dissociation*: Vol. of 0·0630 g. H_2SO_4 and 0·2924 g. H_2O at *N.T.P.* = 14·3 and 362·2 c.c., respectively. Total vol. = 668·8 c.c. $p_{H_2SO_4} = 14{\cdot}3 \times 760/668{\cdot}8 = 16{\cdot}3$ mm. and $p_{H_2O} = 362{\cdot}2 \times 760/668{\cdot}8 = 411{\cdot}1$ mm. Therefore $P = 427{\cdot}4$ mm. *Assuming the acid to be completely dissociated*: Weight of SO_3 in the acid vapour removed = $0{\cdot}0630 \times 80/98 = 0{\cdot}0514$ g., and weight of water removed = $0{\cdot}3554 - 0{\cdot}0514 = 0{\cdot}3040$ g. The corresponding volumes at *N.T.P.* are 14·3 and 376·6 c.c., respectively. Total volume = 683·2 c.c. $p'_{SO_3} = 14{\cdot}3 \times 760/683{\cdot}2 = 15{\cdot}91$ mm. and $p'_{H_2O} = 376{\cdot}6 \times 760/683{\cdot}2 = 419{\cdot}0$ mm. Therefore $P'_{diss.} = 434{\cdot}91$ mm. But $2p_{H_2SO_4} + p_{H_2O} = 443{\cdot}7$ mm. The difference between the results obtained by the two methods of calculation is not serious for the more dilute acids at moderate temperatures. It becomes important at higher temperatures, especially when the concentration exceeds 95%.

Although, for the sake of uniformity, all the experimental results are carried to the first decimal place, this degree of accuracy is not necessarily claimed for each single determination.

At low temperatures the relation between temperature and partial pressure of the water or of the acid vapour was approximately linear in both cases. At higher temperatures, however, the partial pressures increase, with increasing temperature, more rapidly than this simple relationship demands. The variation of the partial pressure with change of temperature can be represented with considerable accuracy by expressions such as that used by Perman for solutions of ammonia in water, or better, by Rankine's equation $\log_{10} p = \alpha - \beta/T - \gamma \log T$. The constants α, β, and γ, in the latter expression were obtained in the usual way from values taken from the smoothed curve.

99·23% H_2SO_4	p	$\alpha = -20{\cdot}0946$;	$\beta = 1695{\cdot}86$;	$\gamma = -9{\cdot}3427$.
98·06% H_2SO_4	$p_{H_2SO_4}$	$\alpha = 8{\cdot}2878$;	$\beta = 4319{\cdot}7$;	$\gamma = -0{\cdot}5166$.
	p_{H_2O}	$\alpha = 20{\cdot}7109$;	$\beta = 5415{\cdot}31$;	$\gamma = 3{\cdot}6353$.
	P	$\alpha = 10{\cdot}8170$;	$\beta = 4518{\cdot}21$;	$\gamma = 0{\cdot}2571$.
95·06% H_2SO_4	$p_{H_2SO_4}$	$\alpha = -106{\cdot}5692$;	$\beta = -4828{\cdot}25$;	$\gamma = -36{\cdot}2945$.
	p_{H_2O}	$\alpha = 22{\cdot}4406$;	$\beta = 4541{\cdot}0$;	$\gamma = 4{\cdot}2726$.
	P	$\alpha = 8{\cdot}4658$;	$\beta = 3516{\cdot}97$;	$\gamma = -0{\cdot}1707$.
91·26% H_2SO_4	$p_{H_2SO_4}$	$\alpha = 48{\cdot}2388$;	$\beta = 7026{\cdot}67$;	$\gamma = 12{\cdot}4310$.
	p_{H_2O}	$\alpha = 65{\cdot}2394$;	$\beta = 7354{\cdot}24$;	$\gamma = 17{\cdot}8856$.
	P	$\alpha = 66{\cdot}8040$;	$\beta = 7483{\cdot}28$;	$\gamma = 18{\cdot}3659$.
89·25% H_2SO_4	$p_{H_2SO_4}$	$\alpha = 75{\cdot}5303$;	$\beta = 8529{\cdot}90$;	$\gamma = 21{\cdot}4699$.
	p_{H_2O}	$\alpha = -32{\cdot}5120$;	$\beta = 216{\cdot}85$;	$\gamma = -13{\cdot}114$.
	P	$\alpha = -33{\cdot}5235$;	$\beta = 155{\cdot}653$;	$\gamma = -13{\cdot}4453$.

TABLE II

	99·23% H_2SO_4.			98·06% H_2SO_4.				
t.	$p_{H_2SO_4}$· obs.	$p_{H_2SO_4}$· calc.	*P.*	$p_{H_2SO_4}$· obs.	$p_{H_2SO_4}$· calc.	p_{H_2O}· obs.	p_{H_2O}· calc.	*P.*
180°	10·0	9·5	19·5	1·5	1·3	0·14	0·12	3·2
185	12·0	11·7	24·0	2·0	1·7	0·18	0·16	4·2
190	14·2	14·0	28·0	2·6	2·2	0·25	0·21	5·1
195	17·2	16·95	34·2	3·2	2·7	0·30	0·27	5·5
200	21·0	20·5	41·0	4·0	3·45	0·35	0·35	8·0
205	24·5	24·6	48·0	4·7	4·3	0·45	0·44	9·7
210	29·0	29·5	58·2	6·2	5·4	0·57	0·55	12·0
215	34·2	35·3	68·5	7·5	6·7	0·72	0·69	15·0
220	41·0	42·1	81·0	8·7	8·3	0·90	0·87	18·2
225	49·0	50·0	94·5	10·5	10·2	1·10	1·07	22·0
230	58·0	60·1	110·5	13·0	12·5	1·32	1·30	27·0
235	67·5	70·6	128·0	15·7	15·3	1·67	1·64	32·7
240	80·0	83·1	149·7	18·7	18·6	2·00	2·01	39·2
245	94·0	97·7	173·0	22·5	22·2	2·40	2·45	46·7
250	111·0	115·5	198·2	27·0	27·1	2·95	2·98	56·0
255	131·0	134·5	227·0	32·2	32·6	3·52	3·61	66·7
260	153·0	158·0	257·5	38·5	39·2	4·22	4·35	78·7
265	179·0	184·3	291·0	46·2	46·7	5·10	5·20	92·5
270	209·5	214·9	327·5	55·5	55·6	5·15	6·25	109·0
275	243·0	250·5	368·0	66·0	66·1	7·42	7·46	127·5
280	282·2	286·6	412·0	78·5	78·1	8·85	8·94	150·2
285	328·0	326·6	459·0	92·7	92·3	10·52	10·50	175·5
290	380·0	389·1	500·2	109·5	109·1	12·47	12·40	205·0
295	440·0	448·4	565·5	130·7	132·7	14·65	14·60	240·5
300	505·2	517·2	626·2	150·1	151·7	17·10	17·12	284·0
305	577·0	596·2	692·0	174·5	174·2	19·95	20·02	336·5
310	659·5	684·7	—	203·5	202·8	23·0	23·35	393·5
315	752·0	—	—	235·0	235·5	26·45	27·14	456·0
320	—	785·1	—	270·0	272·7	30·25	31·50	515·0.

	95·06% H_2SO_4.					91·26% H_2SO_4.				
t.	$p_{H_2SO_4}$· obs.	$p_{H_2SO_4}$· calc.	p_{H_2O}· obs.	p_{H_2O}· calc.	*P.*	$p_{H_2SO_4}$· obs.	$p_{H_2SO_4}$· calc.	p_{H_2O}· obs.	p_{H_2O}· calc.	*P.*
180°	3·2	3·1	11·0	11·7	16·4	0·47	0·51	33·5	31·6	35·0
185	3·5	3·5	12·5	14·3	18·2	0·62	0·66	41·0	39·0	42·0
190	4·0	4·0	16·5	17·5	22·0	0·82	0·84	48·5	49·0	50·0
195	4·5	4·6	20·5	21·3	27·2	1·05	1·07	59·0	58·4	61·2
200	5·1	5·2	25·5	25·8	31·7	1·35	1·35	70·0	70·7	78·1
205	5·9	6·0	31·0	31·1	38·5	1·71	1·70	85·4	85·4	88·0
210	6·7	6·8	37·0	37·3	46·2	2·14	2·13	102·6	102·6	106·2
215	7·7	1·9	44·0	44·5	55·0	2·65	2·63	122·0	120·4	127·2
220	9·1	9·1	53·0	53·0	66·0	3·27	3·24	146·2	144·3	152·0
225	10·3	10·4	62·2	62·5	79·1	3·98	3·98	172·0	170·4	179·5
230	11·9	12·0	74·0	74·1	93·5	4·85	4·84	200·9	199·2	209·5
235	13·7	13·8	87·0	87·2	110·5	5·87	5·88	233·0	233·0	244·0
240	15·6	15·9	102·2	102·1	130·0	7·07	7·12	271·0	270·6	283·0
245	18·1	18·4	119·5	119·4	152·3	8·55	8·55	313·0	312·1	327·0
250	20·9	21·2	139·0	139·0	176·0	10·25	10·22	360·5	360·1	377·2
255	24·3	24·4	160·2	161·3	202·5	12·25	12·16	413·0	413·0	433·5
260	28·1	28·3	185·2	186·5	231·0	14·60	14·45	469·2	470·8	499·5
265	32·5	32·6	213·5	215·0	263·2	17·30	17·01	532·5	535·5	561·2
270	37·9	38·0	245·0	247·1	300·0	20·30	20·02	600·0	604·5	636·5
275	43·6	43·9	281·7	282·3	343·0	24·9	22·42	675·2	684·9	721·0
280	50·2	50·7	323·0	323·8	393·0					
285	58·0	58·4	369·0	369·4	452·2					
290	67·5	67·9	420·0	420·2	522·0					
295	78·5	78·4	478·0	476·3	600·0					
300	91·5	90·7	539·5	538·6	690·0					
305	106·5	105·7	608·0	607·7	—					

TABLE II (*continued*).

89·25% H_2SO_4.

t.	$p_{H_2SO_4}$ obs.	$p_{H_2SO_4}$ calc.	p_{H_2O} obs.	p_{H_2O} calc.	*P.*	*t.*	$p_{H_2SO_4}$ obs.	$p_{H_2SO_4}$ calc.	p_{H_2O} obs.	p_{H_2O} calc.	*P.*
180°	0·45	0·47	69·9	69·4	70·7	225°	3·07	3·12	263·7	265·5	268·0
185	0·60	0·60	82·5	78·8	83·5	230	3·67	3·71	303·0	306·0	307·9
190	0·75	0·75	96·0	94·7	97·3	235	4·34	4·42	347·0	348·9	353·2
195	0·95	0·94	111·7	110·3	113·2	240	5·10	5·22	400·0	403·2	408·0
200	1·18	1·17	128·1	128·4	131·0	245	6·00	6·13	463·0	462·8	471·2
205	1·43	1·44	149·5	148·7	160·9	250	7·13	7·16	534·1	530·0	545·0
210	1·75	1·76	172·0	172·2	174·8	255	8·25	8·35	614·0	605·0	628·5
215	2·12	2·15	198·5	199·4	201·7	260	9·56	9·66	702·0	691·5	723·5
220	2·56	2·59	229·5	230·0	235·5						

The values of the partial pressures and also of the total pressures taken from the smoothed curve, which may be looked upon as the true experimentally determined values, agree closely with the values calculated by means of these equations over the whole range. As was to be expected, the divergences are greatest at low temperatures. The observed and the calculated values of the partial pressures are set out in Table II. The values of *P* are obtained from the observed values on the assumption that the acid vapour undergoes complete dissociation.

On extrapolating the total-pressure curves to 760 mm. the boiling points of the different solutions are obtained.

Data concerning the boiling points of concentrated solutions of sulphuric acid have been given by Marignac (see "Sulphuric Acid and Sulphur Dioxide," Wyld, p. 194) and Beckmann (*Z. physikal. Chem.*, 1905, **53**, 129). The values obtained in this investigation are in good agreement with those obtained by graphical interpolation from the above-mentioned sources. They are shown in Table III.

TABLE III.

Conc. of acid.	B. p. from V. P. curve.	B. p. calc. from equation.	B. p. from other data.	$p_{H_2SO_4}$ at b. p. (mm.).	p_{H_2O} at b. p. (mm.).	B. p. calc. assuming H_2SO_4 vapour dissociated.
99·23%	315·2°	313·8°	310°	—	—	309·75°
98·06	349	352·8	331—338*	678·7	81·3	332·5
95·06	307·5	307·6	300	115	645	302·5
91·26	278·0	278·1	268·7	26·5	733·5	277
89·25	261·5	263·2	257	12·9	747·1	261

* The value 331·7° given by Landolt and Bornstein ("Tabellen," 5th ed., p. 1433) on the authority of Beckmann for the boiling point of pure sulphuric acid clearly should refer to the constant-boiling mixture containing 98·3% H_2SO_4.

In columns 5 and 6 of the above table are given the partial pressures of the water vapour and of the sulphuric acid vapour respectively at the boiling point.

Throughout this work it has been assumed that the sulphuric acid vapour remains undissociated. Whilst this may be approximately true at the lower temperatures, and especially for the more dilute solutions, the vapour in equilibrium with which always contains a large excess of water molecules, at higher temperatures, particularly in the case of the more concentrated solutions, this assumption cannot be justified. According to Dittmar (*Chem. News*, 1870, **20**, 258) pure sulphuric acid in the state of vapour is practically completely dissociated. If this is so, the values obtained for the sulphuric acid partial pressure will be lower than the real partial pressure of the dissociated acid, and the boiling points obtained from these measurements will therefore be too high. The figures given in Table III show this to be the case, although it should be pointed out that this influence, even supposing it to exert its maximum possible effect, is comparatively slight for solutions the concentrations of which lie below 95% H_2SO_4. For example, whereas complete dissociation of the sulphuric acid vapour would increase the total vapour pressure of 98·06% acid at 275° from 73·4 mm. to 127·5 mm., an increase of 73·7%, in the case of 91·26% H_2SO_4 the increase, at the same temperature, amounts to 3% only.

Unfortunately, the extent to which sulphuric acid vapour is dissociated at different temperatures and in the presence of widely varying concentrations of water vapour is not known and, consequently, no systematic correction for this factor can be applied to the values obtained in this research. In Table II values are given for the total vapour pressures, based on the assumption that the sulphuric acid vapour is always completely dissociated. For solutions containing less than 95% H_2SO_4, the increase in the total vapour pressure due to this factor is very slight. In the last column of Table III are given the values obtained for the boiling points when it is assumed that the sulphuric acid vapour is completely dissociated. These figures approach very closely indeed to the generally accepted values.

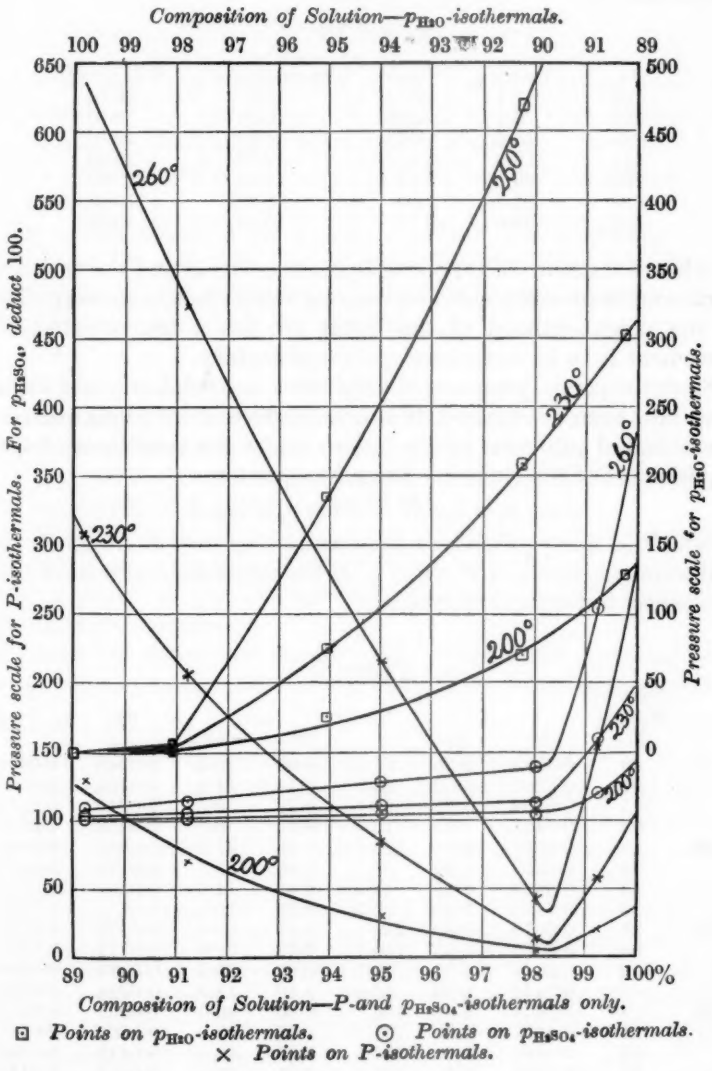
The Variation of the Total Pressure and of the Partial Pressures with the Concentration.

The mode in which the total vapour pressures and the component partial pressures over concentrated sulphuric acid solutions vary when the compositions of these solutions is changed is illustrated in Fig. 2. In this diagram the total pressure, the $p_{H_2SO_4}$- and the p_{H_2O}-isothermals have been drawn for temperatures of 260°, 230°, and 200°. These isothermals are typical.

The form of these curves is striking. In the case of both the $p_{H_2SO_4}$- and the p_{H_2O}-isothermals a sudden and very marked change

of direction occurs when the solution contains 98·2% of sulphuric acid. The total-pressure isothermals exhibit a pronounced minimum at the same composition. This concentration agrees very closely

FIG. 2.


Composition of Solution—p_{H_2O}-isothermals.
100 99 98 97 96 95 94 93 92 90 91 89
650 600 550 500 450 400 350 300 250 200 150 100 50 0
500 450 400 350 300 250 200 150 100 50 0
260°
260°
230°
230°
260°
200°
230°
210°
200°
89 90 91 92 93 94 95 96 97 98 99 100%
Pressure scale for P-isothermals. For $p_{H_2SO_4}$, deduct 100.
Pressure scale for p_{H_2O}-isothermals.
Composition of Solution—P-and $p_{H_2SO_4}$-isothermals only.
⊡ Points on p_{H_2O}-isothermals. ⊙ Points on $p_{H_2SO_4}$-isothermals.
× Points on P-isothermals.

indeed with that of the constant-boiling mixture, which is usually considered to contain 98·3% H_2SO_4.

At this concentration the composition of the liquid and gaseous

phases must be the same and, assuming the vapours in equilibrium with the liquid to behave as perfect gases, the ratio of the two partial pressures should be identical with that of the molecular fractions in the liquid. In Table IV these ratios are compared for a series of temperatures.

TABLE IV.

t.	$p_{H_2SO_4}$.	p_{H_2O}.	$p_{H_2SO_4}/p_{H_2O}$.	$M/(1-M)$.
180°	1·5	0·14	10·7	10·01
200	3·7	0·35	10·5	10·01
220	10·5	0·85	10·23	10·01
240	19·6	1·85	10·05	10·01
260	39·7	3·8	10·45	10·01
280	82·2	8·0	10·27	10·01
300	159·0	15·5	10·30	10·01

When the nature of the partial-pressure curves and the very large variations in pressure which accompany small changes in composition in the neighbourhood of this point are taken into account, the agreement is to be considered quite satisfactory.

Since the partial pressures of both water and sulphuric acid vapour have now been determined, it is possible to test the applicability to concentrated sulphuric acid solutions under the conditions of these experiments of the Duhem—Margules equation

$$d \log p_1/d \log M = d \log p_2/d \log (1 - M)$$

in which p_1 and p_2 represent the partial pressures of sulphuric acid and water vapours and M and $1 - M$ the molecular fractions of these substances in the liquid mixture.

TABLE V.

t.	Conc. of H_2SO_4. %.	M.	p_1.	p_2.	dp_1.	$-dp_2$.	$-\frac{dp_1}{dp_2}$.	$\frac{p_1}{p_2}\cdot\frac{1-M}{M}$.
180°	89	0·5978	0·30	65	0·09	20·0	0·0045	0·0031
	91	0·6257	0·62	43	0·18	11·0	0·0164	0·0086
	93	0·6864	1·02	26	0·22	9·0	0·0246	0·0179
	95	0·7421	1·55	13	0·27	6·0	0·0458	0·0414
200	89	0·5978	0·86	128	0·25	37·0	0·0067	0·0051
	91	0·6257	1·50	80	0·40	23·5	0·0170	0·0112
	93	0·6864	2·37	44·5	0·48	14·5	0·0331	0·0243
	95	0·7421	3·50	20·5	0·60	10·0	0·0610	0·0593
220	89	0·5978	2·50	240	0·45	57·0	0·0079	0·0069
	91	0·6257	3·65	150·7	0·62	36·0	0·0172	0·0111
	93	0·6864	4·90	89·5	0·85	25·5	0·0383	0·0250
	95	0·7421	6·85	46·0	1·10	18·5	0·0594	0·0517
240	89	0·5978	4·86	406	0·80	90·0	0·0089	0·0081
	91	0·6257	6·9	291	1·05	63·0	0·0167	0·0142
	93	0·6864	9·8	186·5	1·65	40·0	0·0412	0·0240
	95	0·7421	13·3	102·0	2·05	37·0	0·0553	0·0453
260	89	0·5978	8·9	727	2·0	142·0	0·0141	0·0082
	91	0·6257	14·0	502	2·61	100·0	0·0261	0·0167
	93	0·6864	20·1	329	3·39	79·0	0·0429	0·0279
	95	0·7421	27·1	188	3·79	68·5	0·0553	0·0501

The integration of this expression involves certain assumptions regarding the relationship between the partial pressure of each component and the vapour pressure of that component in the pure state. If, however, the equation is written in the form

$$-\frac{dp_1}{dp_2}=\frac{p_1}{p_2}\cdot\frac{1-M}{M}$$

it can be tested by substitution of the values obtained from the isothermals. The estimation of dp_1 and dp_2 was carried out graphically by drawing the approximate tangent to the isothermal at the required point. The results obtained are summarised in Table V.

The values obtained for $p_1/p_2.(1-M)/M$ are invariably lower than those for $-dp_1/dp_2$, but in view of the fact that considerable dissociation of the sulphuric acid vapour probably occurs, close agreement was scarcely to be expected.

Summary.

1. The partial pressures of the water vapour in contact with acid–water mixtures containing from 89% to 99·3% of sulphuric acid have been determined at temperatures ranging from 180° to 300° by a method previously described.

2. The previously determined values of the sulphuric acid partial pressures were vitiated by adsorption of acid vapour on the glass wool employed to prevent mechanical transference of liquid, and have been redetermined.

3. Both the water and the sulphuric acid partial pressures, and also the total pressure, can be represented by Rankine's equation

$$\log p = \alpha - \beta/T - \gamma \log T,$$

for which the various constants have been calculated.

4. The boiling points obtained from the total pressure by extrapolation are considerably too high. If, however, it is assumed that complete dissociation of the sulphuric acid vapour occurs, values are obtained which are in good agreement with the accepted values.

5. The $p_{H_2SO_4}$-, p_{H_2O}-, and P-isothermals have been constructed for temperatures of 260°, 230°, and 200°. The P-isothermals exhibit a sharp minimum at a composition 98·2% H_2SO_4. The form of the partial pressure curves is in qualitative agreement with the Duhem–Margules equation. The quantitative agreement, however, is not close, probably on account of dissociation of the acid vapour.

THE UNIVERSITY, CAPE TOWN. [*Received, March 16th*, 1925.]

CCCXCI.—*The Partial Formaldehyde Vapour Pressures of Aqueous Solutions of Formaldehyde. Part II.*

By WILFRID LEDBURY and ETHELBERT WILLIAM BLAIR.

THE investigation of the partial formaldehyde vapour pressures of aqueous formaldehyde solutions, described in Part I (this vol., p. 26), showed that, following a prolonged initial exposure at 15°, equilibrium between the liquid and vapour phases was only gradually attained when the temperature of a solution was subsequently changed to 20° or 0°. An explanation of this was based upon the assumption that a new equilibrium between complex (polymerised, hydrated, etc.) and simple molecules in solution, depending on the temperature, was gradually approached as time elapsed. The presence in aqueous formaldehyde solution of both the polymerised and monomolecular forms is made evident by the work of Auerbach and Barschall (*Arb. Kais. Ges.-A.*, 1905, **22**, 584; *Chem. Centr.*, 1905, II, 1081), who carried out molecular-weight determinations by the cryoscopic method. These determinations indicated that in solutions containing 37—38% (by vol.) of formaldehyde, there probably exist polymerides of complexity greater than trimolecular. Auerbach and Barschall concluded that the equilibrium between the different molecular forms of formaldehyde is reversible, so that the condition of aqueous solutions of formaldehyde, a short time after preparation, depends only on the concentration and temperature. In order to study further the influence of temperature and solution concentration on the partial formaldehyde vapour pressures of aqueous formaldehyde solutions, determinations have been carried out at 35° and 45°, and these new data correlated with those previously obtained at 0° and 20°.

It has been previously pointed out by the authors that methyl alcohol, when present in small amounts (compare the proportion of methyl alcohol to formaldehyde in commercial formalin), considerably enhances the partial formaldehyde vapour pressures of formaldehyde solutions at 20°. Formaldehyde in methyl-alcoholic solution and in a mixture of water and methyl alcohol, containing a large proportion of the latter, has since been investigated in this connexion, and also the effect of the presence of small amounts of the alcohol in formaldehyde solutions at 35° and 45°.

EXPERIMENTAL.

Method and Apparatus.—Aqueous solutions of formaldehyde, free from methyl alcohol, were prepared either by the method of continuous refluxing previously described or by dissolving solid para-

formaldehyde, uncontaminated with methyl alcohol, in boiling water. The solutions so prepared were kept for 2 or 3 weeks at room temperature; it was then assumed that the equilibrium between the different molecular species of formaldehyde in solution had attained a value dependent only on the concentration and temperature of exposure, irrespective of the method of preparation (Auerbach and Barschall, *loc. cit.*; Auerbach and Plüddemann, *ibid.*, 1914, **47**, 116). To ascertain the effect of the presence of small amounts of methyl alcohol on the partial formaldehyde vapour pressures of the solutions, the alcohol, having an acetone content of less than 0·10%, was added to a series of the solutions in such amounts as to provide a constant ratio, CH_4O/CH_2O. For the preparation of formaldehyde in methyl-alcoholic solution, a current of dry nitrogen was passed over paraformaldehyde in a silica tube at 170°. Formaldehyde vapour, carried forward by the gas-stream, was absorbed in methyl alcohol, as free as possible from acetone. The solution was filtered from any insoluble polyoxymethylenes and kept several weeks before use. This solution has an exceptionally irritant action on the membranes of the eyes and nose. Unlike aqueous formaldehyde, it produces this effect after a minute or so.

The formaldehyde content (*ca.* 15%) of this solution was estimated both before and after refluxing with dilute sulphuric acid, and the difference in the values showed that the equivalent of about 5 g. of formaldehyde per 100 c.c. was combined as methylal. When a methyl-alcoholic solution of formaldehyde was prepared by heating an excess of pure paraformaldehyde with methyl alcohol in a sealed tube for 6 hours at 120°, the major portion of the aldehyde in solution was combined as methylal. The free formaldehyde content was 6·63 g. per 100 c.c., whilst the methylal present was equivalent to 12·0 g. per 100 c.c. Refluxing paraformaldehyde with methyl alcohol at the ordinary pressure for 2 days yielded a solution containing 5·16 g. of free formaldehyde and 1·44 g. of combined formaldehyde per 100 c.c.

As in the corresponding determinations at 20° and 0°, the "dynamic" or "flow" method was employed for the series of experiments at 35° and 45°. The apparatus used was similar to that described in Part I, except that a heating unit of 500 watts was substituted for the small carbon-filament lamp. Since accurate estimations of small amounts of formaldehyde are possible by the use of the iodometric method of Romijn (*Analyst*, 1897, **22**, 221; see also *Chem.-Ztg.*, 1901, **25**, 74; *Ber.*, 1898, **31**, 1979; 1901, **34**, 2817), it was necessary to pass volumes of air of only 2 or 3 litres at the most for each vapour pressure determination. During the course of a run, involving several successive determinations on the

same solution, the alteration of the strength of the formaldehyde solution in the "carburettors" was thus made negligible, even in the case of concentrated solutions at 45° (compare Part I). De Waal (*Pharm. Weekblad*, 1907, **44**, 1207; *J. Pharm. Chim.*, 1907, **26**, 498) has shown that in presence of air increase of temperature promotes oxidation of formaldehyde in solution, but that this is slight even at 50°, after an exposure for 400 hours. In the present series of determinations, air was passed at the rate of about 1 litre in 3 hours. All estimations of formaldehyde and methyl alcohol were carried out as previously described, and a similar procedure of experimentation was followed.

Formaldehyde Vapour Pressures of Aqueous Formaldehyde Solutions at 35° and 45°.

For solutions of formaldehyde not containing methyl alcohol, the vapour pressure values at 35°, obtained after the passage of several litres of air (for successive determinations), were slightly higher than those obtained at the outset. This increase, however, was not nearly so marked as at 20°, and the eventual steady maximum was more rapidly reached. Solutions containing methyl alcohol each gave a series of practically identical values from the beginning, and this was also the case with both sets of solutions at 45°. It is evident that, at the temperatures under consideration, the new equilibrium between the various molecular species in solution is attained much more rapidly than at 0° or 20°. The equilibrium values of the formaldehyde vapour pressures for formaldehyde solutions free from methyl alcohol, at 35°, are in Table I, and the corresponding values for solutions containing methyl alcohol ($CH_4O/CH_2O = 0{\cdot}13$) in Table II. (In Tables I—V, g = grams of formaldehyde in 100 c.c. of formalin solution, m_t = mg. of formaldehyde vapour in 1 litre of issuing air at $t°$, and p = partial pressure of formaldehyde vapour in mm. of Hg.). Curves A and B in Fig. 1 represent the relationship between concentration of solution and partial pressure at 35° for pure solutions and for solutions containing methyl alcohol, respectively.

TABLE I.

g	1·09	5·15	11·8	18·6	20·8	31·0	39·5
$m_{35°}$	0·27	1·13	2·06	2·87	3·17	4·27	4·58
p	0·166	0·695	1·29	1·80	1·94	2·48	2·81

TABLE II.

g ($CH_4O/CH_2O = 0{\cdot}13$)	5·24	13·05	23·7	38·3
$m_{35°}$	1·200	2·52	3·97	5·39
p	0·735	1·56	2·45	3·34

The data obtained from solutions at 45° are in Tables III and IV, and the curves showing variation of formaldehyde vapour pressure with solution concentration are plotted in Fig. 2.

TABLE III.

g	10·8	20·4	28·75	39·2
$m_{45°}$	3·77	6·17	7·70	9·12
p	2·30	3·79	4·72	5·60

TABLE IV.

g ($CH_4O/CH_2O = 0·13$)	9·76	19·15	27·0	37·1
$m_{45°}$	3·88	6·62	8·62	10·9
p	2·39	4·07	5·3	6·68

FIG. 2.

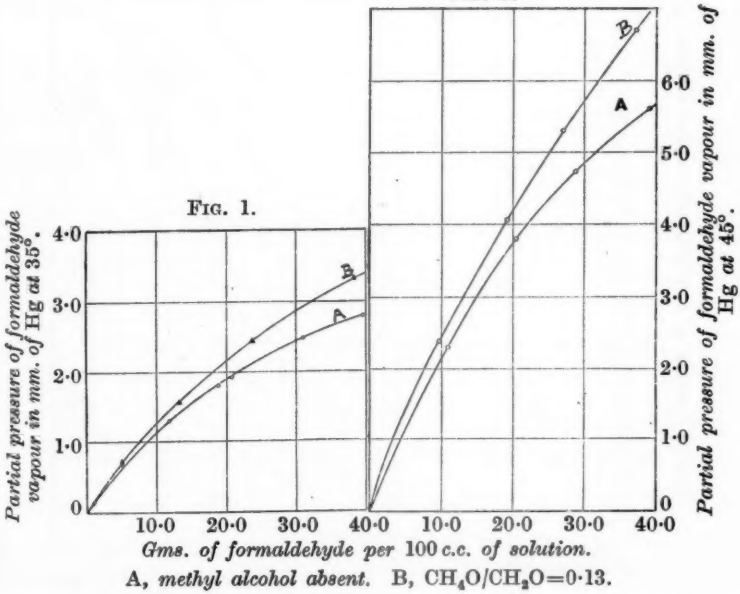


FIG. 1.

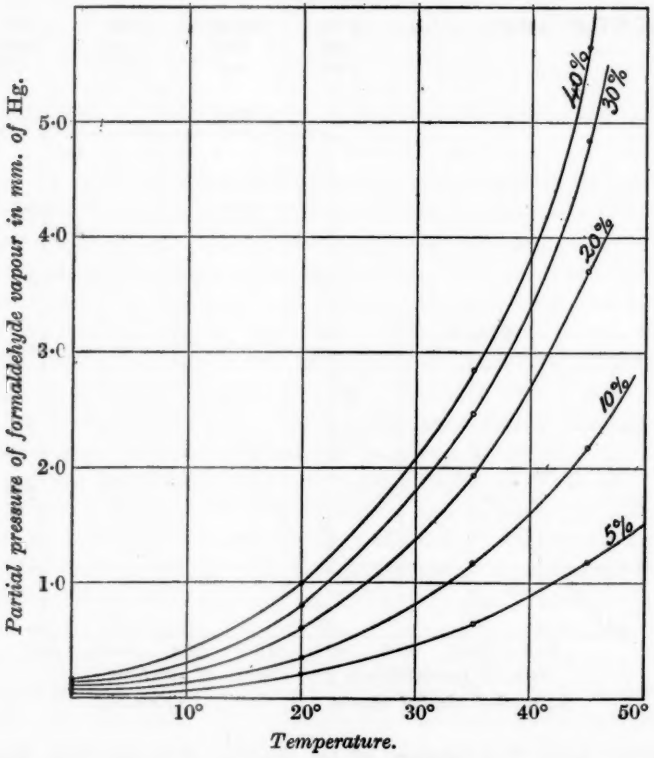
A, *methyl alcohol absent.* B, CH_4O/CH_2O=0·13.

Variation with Temperature of the Partial Formaldehyde Vapour Pressures of Aqueous Formaldehyde Solutions.

From data derived from the curves, drawn to represent the variation of partial formaldehyde vapour pressure with solution concentration at particular temperatures, *viz.*, 0°, 20°, 35°, and 45°, the graphs of Fig. 3 have been plotted to illustrate the manner in which the partial pressures change with temperature. The latter curves are plotted for solutions containing, respectively, 5, 10, 20, 30, and 40 g. of formaldehyde in 100 c.c. It is apparent that the differences between the partial pressures of the more concentrated

solutions at a given temperature are less marked than in the case of the weaker solutions. The data from molecular-weight determinations, the low values of the partial formaldehyde vapour pressures at the temperatures under consideration, and the gradually diminishing dp/dg of the vapour pressure–concentration curves demonstrate the increasing preponderance of polymerides in formalin solutions with increasing concentration. The relatively high

FIG. 3.



concentrations of polymerised formaldehyde in the stronger solutions explains the particular characteristic of the curves referred to above.

When the logarithms of the partial formaldehyde vapour pressures ($\log p$) are plotted against the reciprocals of the absolute temperature ($1/T$) for solutions of given strengths, a series of almost parallel straight lines is obtained. In Fig. 4, the curves indicate the straight-line relationships between $\log_{10} p$ and $1/T$ for solutions having formaldehyde contents of 10, 20, 30, and 40 g. per 100 c.c.,

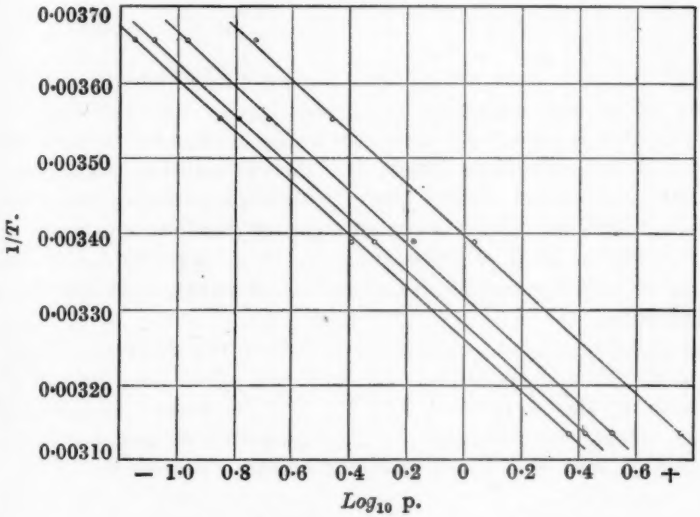
respectively. Thus the formaldehyde partial vapour pressure of any aqueous formaldehyde solution up to a 40% concentration can be expressed, for the temperatures under consideration, by a simplified form of Rankine's equation (*Edinburgh New Phil. J.*, July, 1849) connecting vapour pressure and temperature :

$$\log_{10} p = \alpha - B/T,$$

where $\alpha_{10\%} = 9{\cdot}47$, $\alpha_{20\%} = 9{\cdot}70$, $\alpha_{30\%} = 9{\cdot}81$, $\alpha_{40\%} = 9{\cdot}87$, (approx.) and β (for all solutions up to 40%) = 2905 (approx.).

A straight-line relationship is somewhat deviated from when $\log_{10} p$ for any given solution strength is plotted against T. The formula $\log p = \alpha + \beta T + \gamma T^2 + \ldots.$, which Perman (J., 1903,

FIG. 4.



88, 1168) successfully applied to aqueous solutions of ammonia, was found to be inapplicable to aqueous solutions of formaldehyde.

Methyl-alcoholic Solution of Formaldehyde.—Prior to the determination of the partial formaldehyde vapour pressure at 20° of a methyl-alcoholic solution (15·9 g. CH_2O per 100 c.c.), blank determinations were carried out on a sample of the methyl alcohol employed, since, although this alcohol was the purest obtainable, it was not quite free from acetone (less than 0·10%). At 20°, the blank values were equivalent to about 0·1 mm. of formaldehyde, estimations being carried out iodometrically. Further vapour-pressure determinations have been carried out at 20° and 0° on formaldehyde in methyl alcohol–water solution, the alcohol being present in preponderating amount. This latter solution was obtained by

diluting with water the original 15% methyl-alcoholic solution in order to obtain a liquor containing 10 g. of free formaldehyde per 100 c.c. Blanks were performed at 20° and 0° on a mixture of methyl alcohol and water, in which the proportions of the two components were the same as in the formaldehyde solution examined. The data obtained are in Table V: solution *A* contained 15·97 g. of free formaldehyde (equivalent of 5·0% formaldehyde as methylal) in 100 c.c. of methyl-alcoholic solution; solution *B* contained 10 g. of free formaldehyde, 59 g. of methyl alcohol, and 26·7 g. of water in 100 c.c.

TABLE V.

Solution.	*t*.	m_r.	*p*.
A	20°	3·68	2·27
B	20	1·93	1·16
B	0	0·390	0·234

It will be seen that at 20° the partial formaldehyde vapour pressure of an approximately 15% solution of formaldehyde in methyl alcohol is almost *five* times the value of that for an aqueous solution of corresponding strength. For a solution containing about 60% of methyl alcohol there is an approximately threefold increase at both 20° and 0° over an aqueous solution containing a corresponding amount of formaldehyde (10 g. per 100 c.c.). In all cases, practically constant vapour pressure values were obtained from the outset.

Since methylal vapour, carried forward from the methyl-alcoholic solution to the absorption worms, does not affect the iodometric estimation of the formaldehyde fixed by the water (Bergstrom, *J. Amer. Chem. Soc.*, 1923, **45**, 2150), the figure obtained represents the partial vapour pressure of uncombined formaldehyde in methyl-alcoholic solution.

If it be assumed that the methylal (which is present to the extent of the equivalent of 5 g. of formaldehyde per 100 c.c. of 15% methyl-alcoholic solution) does not exert a *very* pronounced influence, in its solvent capacity, on the partial vapour pressure of the free formaldehyde in solution, then it is found that the application of the simple mixture rule to a 15% aqueous solution, in which $CH_4O/CH_2O = 0·13$, by no means accounts for the enhanced value at 20° brought about by the addition of the alcohol to the original aqueous formalin, *i.e.*, from 0·49 to 0·59 mm. Hg.

It has been pointed out that the removal of methyl alcohol from commercial formalin (40% by vol.) increases the tendency of paraformaldehyde to separate from solution. Experiments have shown, however, that paraformaldehyde is more readily soluble in water than in methyl alcohol; thus the precipitation of paraformaldehyde

from formalin, which has been freed from methyl alcohol, cannot be attributed to the removal of a constituent having a greater solvent capacity for formaldehyde. It therefore appears that the presence of methyl alcohol in aqueous formaldehyde solutions must bring about an alteration of the equilibrium between simple and complex molecules in such a way as to enhance considerably the concentration of mono-molecular formaldehyde. The consequent decrease in the concentration of the polymerides naturally decreases their liability to precipitation as paraformaldehyde. Such an effect on the above-mentioned equilibrium serves to explain why methyl alcohol, present in small amount in an aqueous formaldehyde solution, increases the partial formaldehyde vapour pressure to an extent beyond that anticipated from the application of the simple mixture rule. It is here assumed, as hitherto, that the formaldehyde vapour pressure is almost entirely dependent on the concentration of the simple molecular form of the aldehyde.

Summary.

The partial formaldehyde vapour pressures of aqueous solutions of formaldehyde, free from methyl alcohol, have been determined by the dynamic method at 35° and 45°. Corresponding determinations, carried out on solutions of formaldehyde containing small amounts of methyl alcohol ($CH_4O/CH_2O = 0{\cdot}13$), have shown that the influence of the alcohol in enhancing the vapour pressures is similar to that noted at 20°. The effect of increased temperature in bringing about a more rapid adjustment of equilibrium conditions has also been shown.

From the vapour pressure values a relationship connecting functions of the vapour pressure and the temperature has been derived.

The partial formaldehyde vapour pressure of a methyl-alcoholic solution of formaldehyde has been determined, and the influence of methyl alcohol on the formaldehyde vapour pressures of aqueous formaldehyde solutions considered.

The authors desire to express their thanks to the Department of Scientific and Industrial Research and to the Admiralty for permission to publish these results.

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CCCXCII.—*Transformations of the Sugar Nitrates.*

By JOHN WALTER HYDE OLDHAM.

ALTHOUGH the nitrates of the sugar group are, as a rule, definitely crystalline and easily adaptable to synthetical operations, little use seems to have been made of them since they were studied by Will and Lenze (*Ber.*, 1898, **31**, 68) and Koenigs and Knorr (*Ber.*, 1901, **34**, 957).

When 2 : 3 : 5-trimethyl glucosan, dissolved in chloroform, is acted on by fuming nitric acid under the conditions described in the experimental part, *trimethyl glucose dinitrate* is obtained. The result is striking, particularly as the action of the same reagent on 1 : 6-diacetyl 2 : 3 : 5-trimethyl glucose yielded a syrup which failed to crystallise. Trimethyl glucose dinitrate has no action on Fehling's solution, either before or after acid hydrolysis. The nitrate group in position 1 can be replaced by methoxyl by boiling with methyl alcohol in presence of barium carbonate, the reaction yielding *trimethyl methylglucoside* 6-*mononitrate*. This mononitrate is converted on hydrolysis into the same trimethyl methylglucoside as is obtained from trimethyl glucosan, and the nitrate group was definitely allocated to the 6 position by the fact that, on treatment with sodium iodide, the same trimethyl methylglucoside iodohydrin was readily produced as that already obtained from Fischer's acetodibromoglucose (Irvine and Oldham, this vol., p. 2729). This sequence of changes indicates that the nitrate group possesses considerable reactivity, yet the compound was recovered unchanged (as was also methylglucoside 6-mononitrate) when heated with alcoholic ammonia, as described by Wallach (*Ber.*, 1881, **14**, 422).

In the parallel case of triacetyl glucosan, the action of fuming nitric acid was more complex and a yellow syrup showing a high nitrogen content was invariably produced, together with *triacetyl glucose* 1 : 6-*dinitrate*, which was isolated in fair yield. The compound had likewise no action on Fehling's solution before or after acid hydrolysis, but was readily converted into derivatives of different types. On boiling in glacial acetic acid solution with sodium acetate, it was converted into *tetra-acetyl glucose* 6-*mononitrate*; and this on hydrolysis yielded a *tetra-acetyl glucose*, isomeric with that already obtained by Fischer, in that the sixth hydroxyl group in place of the first is unsubstituted. Further, although triacetyl glucose dinitrate reacted with methyl alcohol only with great difficulty, yields of 50—60% of the corresponding *triacetyl methylglucoside* 6-*mononitrate* were obtained. This compound was converted into *triacetyl methylglucoside* on hydrolysis and into

triacetyl methylglucoside 6-*iodohydrin* on treatment with sodium iodide in acetone in the manner described by Irvine and Oldham (*loc. cit.*).

Methylglucoside 6-*mononitrate* obtained by the action of ammonia on the corresponding acetyl derivative could not be isolated, as it could not be separated from acetamide. By the action of dimethylamine and removal of the acetodimethylamide, however, the mononitrate of the parent glucoside was isolated as a syrup which failed to crystallise. By means of the silver oxide reaction, this compound was converted into the trimethyl methylglucoside 6-mononitrate already described, thus establishing the constitution of the complete series of new derivatives. Triacetyl methylglucoside 6-iodohydrin, on treatment with dimethylamine in the manner already described, gave a somewhat poor yield of *methylglucoside* 6-*iodohydrin*. Finally, incidental evidence was obtained, in the course of large-scale preparations of triacetyl methylglucoside 6-mononitrate, that degradation to the pentose series had taken place to a limited extent.

Synthetical and constitutional studies based on the method of nitrate formation now communicated are in progress.

Experimental.

2 : 3 : 5-*Trimethyl Glucose* 1 : 6-*Dinitrate*.—A solution of trimethyl glucosan (5 g.) in a mixture of 60 c.c. of fuming nitric acid and 40 c.c. of chloroform containing a few grams of phosphorus pentoxide was kept for 19 hours at the ordinary temperature. The specific rotation increased from $-64°$ to $+140·7°$, calculated on the change in concentration due to the addition of two nitrate groups. The mixture was poured slowly with constant stirring into ice, the lower layer separated, washed once with ice-cold water, and taken to dryness below 60° in a vacuum. The *dinitrate* crystallised from absolute alcohol in colourless needles, m. p. 86° (Found : OMe, 30·3; N, 9·1. $C_9H_{16}O_{10}N_2$ requires OMe, 29·8; N, 9·0). The compound is sparingly soluble in alcohol, insoluble in water or light petroleum, and soluble in other solvents. $[\alpha]_D$ + 149·3° in chloroform (*c*, 2·3193), + 151·7° in acetone (*c*, 1·463), + 144·8° in methyl alcohol (*c*, 1·508), and + 147·2° in a mixture of 60% of fuming nitric acid and 40% of chloroform by volume (*c*, 2·915).

Trimethyl Methylglucoside 6-*Mononitrate*.—The dinitrate was boiled in 5% solution in methyl alcohol for ½ hour in presence of barium carbonate. The product, isolated in the usual manner (yield 90%), was drained on a tile and recrystallised from light petroleum; it then melted at 53—54°, n_D of the superfused substance = 1·4565 (Found : C, 42·7; H, 6·7; OMe, 44·1; N, 4·95. $C_{10}H_{19}O_8N$ requires C, 42·7; H, 6·8; OMe, 44·1; N, 5·0%). The

mononitrate is insoluble in water, but soluble in all other solvents. $[\alpha]_D$ — 5·2° in chloroform (*c*, 2·0653), — 4·4° in acetone (*c*, 3·5845), and — 1·3° in methyl alcohol (*c*, 3·3413).

Conversion of Trimethyl Methylglucoside 6-Mononitrate into Trimethyl Methylglucoside.—The compound was hydrolysed by boiling with iron dust in glacial acetic acid, in not more than 5% concentration, until a few drops of the liquid gave no trace of blue colour on standing for some time with a strong solution of diphenylamine in concentrated sulphuric acid. (This reaction is given by all these compounds, and constitutes an extremely delicate test for the presence of a nitrate group.) The solution was then filtered, the residue washed with glacial acetic acid, and the filtrate poured into water containing a fair quantity of dissolved sodium acetate, the object of which was to suppress the hydrogen chloride set free by the chloroform with which the solution was repeatedly extracted. The trimethyl methylglucoside thus removed, on recrystallisation from light petroleum, showed the correct melting point and mixed melting point. The yield was good.

Conversion into the Corresponding Iodohydrin.—On treating the mononitrate with sodium iodide in the manner already described (Irvine and Oldham, this vol., p. 2729), a good yield of crystals was obtained, m. p. 31—33°, which showed no depression on mixing with a sample of the authentic iodohydrin.

Preparation of Triacetyl Glucose 1 : 6-Dinitrate.—The best conditions as yet found are the following: Triacetyl glucosan (5 g.) was dissolved in a mixture of 30% of chloroform with 70% of redistilled nitric acid * by volume, solid nitrogen pentoxide (10 g.) added, and the whole made up to 100 c.c. with chloroform and kept at the ordinary temperature for about 110 hours. The specific rotation of the solution was then about + 138°. Sometimes the liquid separates into two layers; should these not disappear towards the end of the reaction, the system can be made homogeneous by the addition of a small measured amount of fuming nitric acid. The product was isolated in the manner described for the corresponding methylated derivative and washed with cold absolute alcohol (yield about 65%). On recrystallisation from hot absolute alcohol, this yield was diminished by nearly half and the product melted at 132—133°. The substance is insoluble in water, light petroleum, or cold ethyl alcohol, sparingly soluble in ether or cold methyl alcohol,

* In this paper, the expression "fuming nitric acid" refers to the product obtained by distilling ordinary concentrated nitric acid over its own volume of concentrated sulphuric acid. "Redistilled nitric acid" refers to a product, *d* 1·54, obtained by distilling "fuming nitric acid" over twice its volume of concentrated sulphuric acid.

and soluble in other solvents. The rotation of the pure compound in a mixture of fuming nitric acid and chloroform similar to that used in the preparation was $[\alpha]_D + 144{\cdot}2°$ for $c = 5{\cdot}0$. The substance has not been analysed, as it is difficult to obtain a perfectly pure specimen, but in view of the derivatives into which it can be transformed there can be little doubt that it consists of *triacetyl glucose* 1 : 6-*dinitrate*.

Tetra-acetyl Glucose 6-*Mononitrate*.—The dinitrate was boiled for 1—1½ hours with a mixture of acetic acid, acetic anhydride, and sodium acetate. If the dinitrate was pure, scarcely any colour was developed; but if not, the solution coloured deeply. In the former case, the reaction was practically quantitative, as was shown by the specific rotation falling from + 144° to + 23·3°, the corresponding value of the pure substance in acetic acid being + 23·2°. The product was poured into water, when about 80% of it separated almost immediately in a crystalline condition; the remainder, however, sometimes took several days to separate. The product after recrystallisation from absolute alcohol melted at 142—143°, reduced Fehling's solution strongly on boiling, was insoluble in water or light petroleum, sparingly soluble in ether or alcohol, and soluble in other solvents (Found: C, 42·55; H, 5·0; N, 3·65. $C_{14}H_{19}O_{12}N$ requires C, 42·7; H, 4·8; N, 3·6%). $[\alpha]_D + 23{\cdot}2°$ in glacial acetic acid (*c*, 2·494) and + 27·2° in chloroform (*c*, 2·038).

Tetra-acetyl Glucose.—The 6-mononitrate was hydrolysed with iron dust in glacial acetic acid exactly as described in the case of the corresponding methylated compound. *Tetra-acetyl glucose* crystallised from ether in colourless needles, m. p. 126·5—127·5°, $[\alpha]_D + 9{\cdot}8°$ in chloroform (*c*, 0·816) (Found: $C_2H_4O_2$, after allowance for the alkali used by the reducing sugar, 68·7. Calc., $C_2H_4O_2$, 68·9%). The substance is insoluble in cold water or light petroleum, sparingly soluble in ether, soluble in hot water and in organic solvents generally.

The above reaction is rather uncertain, as sometimes the product failed to crystallise.

Triacetyl Methylglucoside 6-*Mononitrate*.—Triacetyl glucose dinitrate, unlike both acetonitroglucose and the corresponding methylated derivative, reacted only with great difficulty with methyl alcohol in presence of barium carbonate, even when a small quantity of pyridine was added as recommended by Koenigs and Knorr (*loc. cit.*). On boiling the mixture for 24 hours, the specific rotation of the solution became constant at + 5·0°. The solution was filtered, and the solid well washed with chloroform. The washings were used to dissolve the residue left on evaporation of the methyl-alcoholic filtrate, in order to purify it from traces of barium nitrate. After removal of the chloroform, the red residue, crystallised twice

from absolute alcohol, melted at 133·5—134·5° (yield 50—60%), and was insoluble in water or light petroleum, sparingly soluble in ether or cold ethyl or methyl alcohol, and soluble in other solvents (Found : C, 42·8; H, 5·35; N, 3·8; OMe, 8·6; $CH_3 \cdot CO_2H$, 66·0. $C_{13}H_{19}O_{11}N$ requires C, 42·7; H, 5·2; N, 3·8; OMe, 8·5; $CH_3 \cdot CO_2H$, 65·7%). $[\alpha]_D$ — 14·3° in chloroform (*c*, 5·964) and — 14·1° in acetone (*c*, 2·6913). If the substance is boiled with methyl-alcoholic sodium methoxide, the specific rotation falls to — 115°, allowance being made for the change in concentration due to loss of acyl groups, which corresponds to the formation of about 80% of Fischer's anhydro-methylglucoside.

Triacetyl Methylglucoside.—On hydrolysing the nitrate with iron dust in glacial acetic acid in the manner already described, *triacetyl methylglucoside* was obtained, in good yield, in colourless crystals, melting after recrystallisation from ether at 134—134·5°; $[\alpha]_D$ in chloroform = — 19·1° for $c = 1{\cdot}514$ (Found : OMe, 9·5; $CH_3 \cdot CO_2H$, 54·6. $C_{13}H_{20}O_9$ requires OMe, 9·6; $CH_3 \cdot CO_2H$, 56·2%). The compound is insoluble in cold water or light petroleum, but soluble in other solvents including hot water.

Methylglucoside 6-*Mononitrate.*—Triacetyl methylglucoside 6-mononitrate was treated with a 5% methyl-alcoholic solution of dimethylamine, and the acetodimethylamide produced was distilled off in a vacuum at 100°; the residual syrup failed to crystallise (Found : N, 5·9; HNO_3, 25·7. $C_7H_{13}O_8N$ requires N, 5·85; HNO_3, 26·3%). A specimen of the substance was twice methylated by the silver oxide reaction; the product crystallised on nucleation with trimethyl methylglucoside 6-mononitrate obtained as described above. After draining on a tile and recrystallisation from light petroleum, the compound showed the correct melting point and mixed melting point, thus proving the constitution of this series of substances.

Triacetyl Methylglucoside 6-*Iodohydrin.*—For the sake of comparison, triacetyl methylglucoside 6-mononitrate was treated with sodium iodide in acetone in the manner already described. The product, after recrystallisation from aqueous alcohol, consisted of colourless needles, m. p. 111—112·5°, which were insoluble in water or light petroleum but soluble in other solvents. The yield was poor [Found : OMe, 7·4; I, 28·0; $CH_3 \cdot CO_2H$ (I being calculated as $CH_3 \cdot CO_2H$), 56·4. $C_{13}H_{19}O_8I$ requires OMe, 7·2; I, 29·5; $CH_3 \cdot CO_2H$, 55·8%). The specific rotation in chloroform was + 0·9° for $c = 3{\cdot}027$.

Methylglucoside 6-*Iodohydrin.*—On treatment with dimethylamine in the manner already described, the preceding triacetyl derivative was converted into the parent glucoside in bad yield. The product, which consisted when pure of colourless crystals, but

was usually slightly pink, melted at 157—158°, was insoluble in ether or light petroleum, very sparingly soluble in chloroform, slightly more soluble in acetone, and soluble in other solvents. The best recrystallising medium was a mixture of chloroform and ethyl acetate (Found: OMe, 10·3; I, 41·7. $C_7H_{13}O_5I$ requires OMe, 10·1; I, 41·7%). $[\alpha]_D$ in chloroform = − 16·1° for $c = 1·677$.

Acetonitropentose.—On taking to dryness the mother-liquors from the recrystallisation of triacetyl methylglucoside 6-mononitrate, boiling for ½ hour with acetic anhydride and sodium acetate, and pouring into water, a precipitate was obtained which, after very many recrystallisations from absolute alcohol, melted at 168—169°. The compound did not reduce Fehling's solution, and was at first thought to be the α-form of triacetyl methylglucoside 6-mononitrate. It contained no methoxyl, however, and the analytical figures are in close agreement with those required for a triacetyl pentose mononitrate (Found: C, 41·2; H, 4·7; N, 4·2. $C_{11}H_{15}O_{10}N$ requires C, 41·1; H, 4·7; N, 4·4%). The substance had the same solubilities as triacetyl glucose dinitrate, and showed specific rotation in chloroform = + 92·0° for $c = 1·214$.

The author wishes to express his indebtedness to the Carnegie Trust, and also to Principal Sir James C. Irvine for much valuable advice and for the kindly interest he has always shown in the work.

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CCCXCIII.—*Lead Dihydride and Lead Tetrahydride.*

By EDWARD JOSEPH WEEKS.

SOLID hydrides of arsenic (*Chem. News*, 1924, **129**, 31), antimony (this vol., p. 1069), and bismuth (*ibid.*, p. 1799) having been prepared, the existence of a solid lead hydride was investigated. To a solution of alkali plumbite made from lead acetate and caustic soda or potash, pure aluminium foil was added. The grey deposit obtained was washed many times with caustic potash solution and finally with water until the washings were neutral. It was filtered off, and dried in a vacuum desiccator over sulphuric acid for 3—5 days, both operations being performed in an atmosphere of hydrogen. The action follows the equation $2KHPbO_2 + 2Al = 2KAlO_2 + Pb_2H_2$. The deposit contained lead and hydrogen only, and on heating in a vacuum gave off hydrogen and left metallic lead. Details of the method of analysis have already been given for bismuth (*loc. cit.*). 0·3253 G. gave 20 c.c. of H_2 measured at *N.T.P.* and 0·3243 g. of

Pb. H, 0·5; Pb, 99·1%. 0·1504 G. gave 10 c.c. of H_2 at *N.T.P.* and 0·1422 g. of Pb. H, 0·6; Pb, 99·5%. On combustion, 1·9550 g. gave 0·0662 g. of H_2O. H, 0·5% (Pb_2H_2 requires Pb, 99·5; H, 0·5%).

Lead dihydride heated in a tube in the absence of air gave lead and hydrogen only. No trace of PbH_4 appeared to be formed, as no lead deposit could be obtained on heating the issuing gas. The dihydride oxidises rapidly in the air and therefore must be kept in an inert gas. Fused potassium nitrate reacted vigorously with it (as with As_2H_2; Sb_2H_2; Bi_2H_2), but only slowly oxidised finely divided lead.

To obtain the tetrahydride, first prepared by Paneth, the dihydride was heated in a silica tube in an atmosphere of pure hydrogen, and the issuing gas was passed through a heated tube; a deposit of lead was then obtained. With hydrogen alone, no deposit was formed and hence it is concluded that the reduction of Pb_2H_2 follows the equation $Pb_2H_2 + 3H_2 = 2PbH_4$.

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CCCXCIV.—*Complex Formation in Lead Nitrate Solutions. Part II. The Quaternary System Potassium Nitrate–Lead Nitrate–Barium Nitrate–Water.*

By SAMUEL GLASSTONE and ERNEST J. RIGGS.

THE primary object of the present work was to investigate the quaternary system lead nitrate–barium nitrate–potassium nitrate–water at 25° and at 50°, and hence it was required to have a knowledge of the three ternary systems KNO_3–$Pb(NO_3)_2$–H_2O, KNO_3–$Ba(NO_3)_2$–H_2O and $Pb(NO_3)_2$–$Ba(NO_3)_2$–H_2O, at the same temperatures. The first of these three systems has been investigated by Glasstone and Saunders (J., 1923, **123**, 2134) at 25° and 50°; the second has been examined at 9·1°, 21·1° and 35° by Findlay, Morgan, and Morris (*ibid.*, 1914, **105**, 779) and to a limited extent at 25° by Foote (*Amer. Chem. J.*, 1904, **32**, 251); the 25°-isothermal for the third system was investigated by Fock (*Z. Kryst.*, 1897, **28**, 337). Before the quaternary system was examined, therefore, Foote's measurements on the ternary system KNO_3–$Ba(NO_3)_2$–H_2O at 25° were extended and the 50°-isotherm was determined completely; Fock's work at 25° was repeated because this author did not use the Schreinemakers residue method for the determination of the composition of the solid phase, and the 50°-isotherm for the system

$Pb(NO_3)_2$–$Ba(NO_3)_2$–H_2O was also determined. Finally, the quaternary system $Pb(NO_3)_2$–$Ba(NO_3)_2$–KNO_3–H_2O was investigated as completely as possible at 25° and 50°. It was hoped to obtain through this investigation further evidence for the existence of a double or complex salt of lead nitrate and potassium nitrate, the presence of which has already been suspected in solutions containing these two salts (see Glasstone and Saunders, *loc. cit.*). Lead and barium nitrates have an almost identical crystal structure (Vegard, *Z. Physik*, 1922, **9**, 395) and separate from solutions containing both salts as a continuous series of mixed crystals; further, potassium and barium nitrates form a double salt, $2KNO_3,Ba(NO_3)_2$ (Foote, *loc. cit.*), and consequently it was thought possible that when this double salt separated from a solution containing lead, barium, and potassium nitrates there might be a tendency for a potassium nitrate–lead nitrate double salt with a similar structure, which has no stable existence at the ordinary temperature, to separate with it as a mixed crystal. This idea was based on the well-known existence of $CuSO_4,7H_2O$ in the form of a mixed crystal with $FeSO_4,7H_2O$, and the recent preparation by Richards and Meldrum (*J. Amer. Chem. Soc.*, 1921, **43**, 1543) of $Na_2SO_4,4H_2O$, which does not exist by itself, as a mixed crystal with $Na_2CrO_4,4H_2O$. The results of the present work indicate that lead nitrate can exist in some form which is isomorphous with either potassium nitrate or with the potassium–barium double nitrate; the most probable form is as the double salt $2KNO_3,Pb(NO_3)_2$, which has no stable existence at the ordinary temperature but might separate as a mixed crystal with $2KNO_3,Ba(NO_3)_2$.

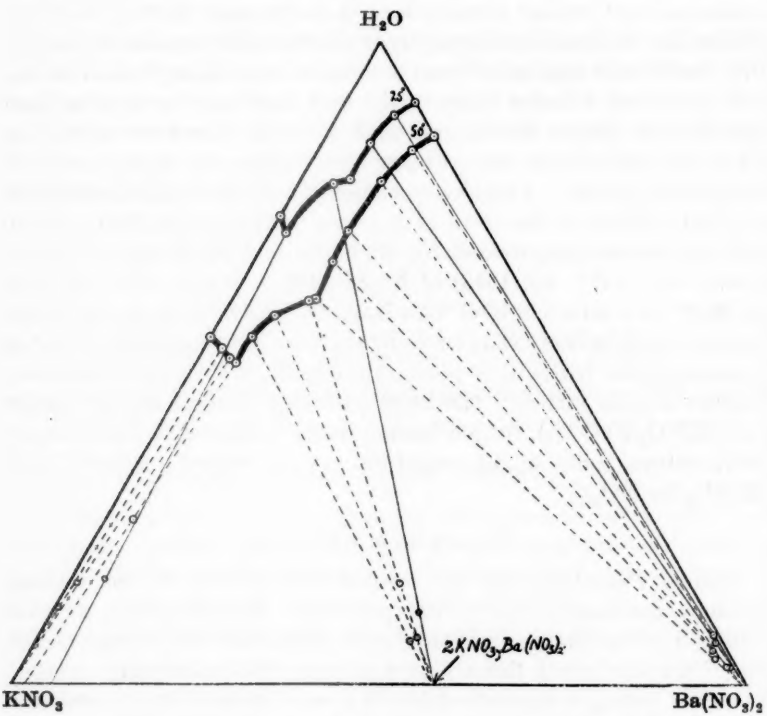
Experimental.

General Procedure.—In the case of the second of the ternary systems mentioned above, the procedure was the same as that followed in the first part of this work (Glasstone and Saunders, *loc. cit.*); for the third ternary system and the quaternary system, however, owing to the deposition of mixed crystals, it was essential that very little of the solid phase should separate, and consequently the mixed solids were made to dissolve in water at a temperature just above that at which the isotherm was being determined and the solution was stirred in a thermostat until sufficient solid for analysis had separated as the result of evaporation.

Method of Analysis.—The amounts of water in the saturated solutions and wet solids were determined by drying known weights first on the water-bath, then in an air-oven at 110°, and finally at 130°. The dry solid was then dissolved in water, made up to a known volume, and an aliquot portion taken for analysis. If the

solution contained only potassium and barium nitrates, the barium was precipitated directly as sulphate with sulphuric acid, and the barium sulphate was washed, dried, and weighed. When the solution for analysis contained lead and barium nitrates only, hydrogen sulphide was passed into the warmed solution until all the lead was precipitated; the precipitate of lead sulphide was filtered off, washed with a solution of hydrogen sulphide, and the barium in the filtrate estimated as sulphate. The amount of lead was usually

FIG. 1.



found by difference, but in several cases the sulphide was dissolved in hot dilute nitric acid and the lead estimated as sulphate by the method described in Treadwell's "Quantitative Analysis" (1919, p. 174). When the solution to be analysed contained all three nitrates, both the lead and the barium were determined by the methods described above, and the potassium was obtained by difference. The analytical method was tested beforehand on mixtures of known weights of the various nitrates and found to be quite satisfactory.

Results.—These are all given as percentages.

KNO_3–$Ba(NO_3)_2$–H_2O at 25°.

Solution.			Rest.			
KNO_3.	$Ba(NO_3)_2$.	H_2O.	KNO_3.	$Ba(NO_3)_2$.	H_2O.	Solid phase.
27·39	0·00	72·61	—	—	—	KNO_3
27·67	2·44	69·89	78·65	4·84	16·51	KNO_3 + D.S.
17·14	4·88	77·98	39·31	49·67	11·02	D.S.
*14·8	6·6	78·6	—	—	—	D.S. + $Ba(NO_3)_2$
9·13	6·57	84·30	1·18	92·26	6·56	$Ba(NO_3)_2$
3·80	7·72	88·48	1·05	91·18	7·77	,,
0·00	9·28	90·72	—	—	—	,,

D.S. refers to the double salt $2KNO_3,Ba(NO_3)_2$.
* Taken from Foote, *loc. cit.*

KNO_3–$Ba(NO_3)_2$–H_2O at 50°.

Solution.			Rest.			
KNO_3.	$Ba(NO_3)_2$.	H_2O.	KNO_3.	$Ba(NO_3)_2$.	H_2O.	Solid phase.
45·45	2·34	52·21	87·05	0·65	12·30	KNO_3
44·88	4·22	50·90	84·20	1·25	14·55	,,
44·66	5·11	50·23	74·36	3·87	21·77	KNO_3 + D.S.
40·31	5·64	54·05	42·78	50·55	6·67	D.S.
35·75	6·99	57·26	42·38	46·05	11·57	,,
30·08	10·16	59·76	41·56	50·93	7·51	,,
28·86	10·81	60·33	2·18	92·55	5·27	D.S. + $Ba(NO_3)_2$
24·14	10·43	65·43	0·02	95·39	4·59	$Ba(NO_3)_2$
18·76	10·14	71·10	2·28	93·48	4·24	,,
10·53	10·92	78·55	1·33	95·39	3·28	,,
3·93	12·73	83·34	1·07	95·85	3·08	,,
0·00	14·63	85·37	—	—	—	,,

The results obtained for this system are represented in Fig. 1.

$Pb(NO_3)_2$–$Ba(NO_3)_2$–H_2O at 25°.

Solution.			Rest.			Solid phase.	
$Pb(NO_3)_2$.	$Ba(NO_3)_2$.	H_2O.	$Pb(NO_3)_2$.	$Ba(NO_3)_2$.	H_2O.	$Pb(NO_3)_2$.	$Ba(NO_3)_2$.
34·60	1·39	64·01	81·83	11·26	6·91	87·54	12·46
31·13	2·65	66·22	66·90	18·90	14·20	76·56	23·44
22·73	4·23	73·04	38·08	56·67	5·25	39·27	60·73
16·21	5·29	78·50	—	—	—	—	—
8·96	6·66	84·38	15·06	80·02	4·92	15·44	84·56
6·26	7·31	86·43	10·15	84·28	5·57	10·42	89·58
1·63	8·64	89·73	3·44	89·54	7·02	3·59	96·41

$Pb(NO_3)_2$–$Ba(NO_3)_2$–H_2O at 50°.

Solution.			Rest.			Solid phase.	
$Pb(NO_3)_2$.	$Ba(NO_3)_2$	H_2O.	$Pb(NO_3)_2$.	$Ba(NO_3)_2$.	H_2O.	$Pb(NO_3)_2$.	$Ba(NO_3)_2$.
40·82	2·57	56·61	77·06	9·54	13·40	88·31	11·69
37·78	3·83	58·39	63·40	26·10	10·50	69·02	30·98
29·31	6·32	64·37	40·31	55·14	4·55	41·25	58·75
17·05	9·12	73·83	—	—	—	—	—
10·34	11·05	78·61	8·92	83·87	7·21	8·78	91·22
5·72	12·68	81·60	6·60	87·70	5·70	6·67	93·33

The results obtained for this system are represented in the usual manner in Fig. 2. In the columns headed "solid phase" are given

FIG. 2.

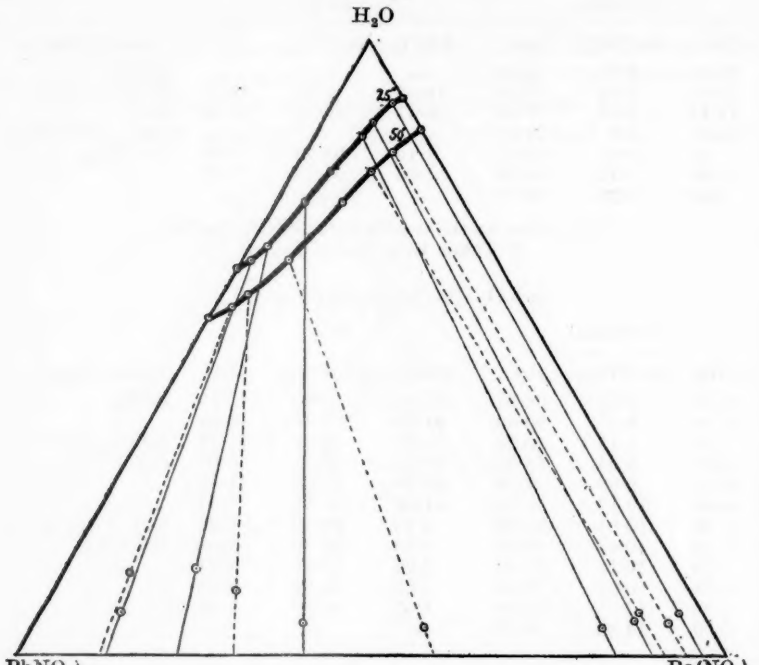
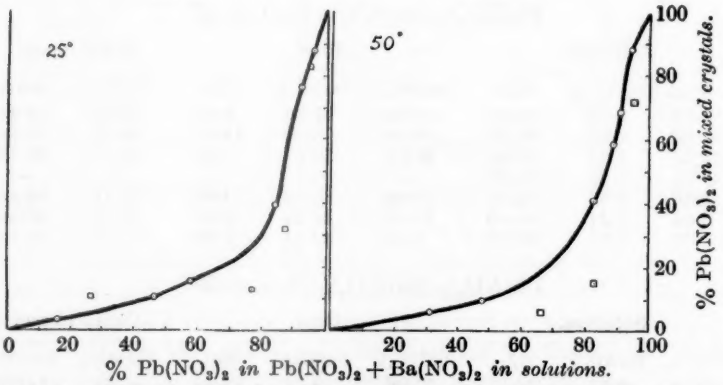


FIG. 3.

FIG. 4.



Circles represent points from the ternary system; squares, points from the quaternary system.

the compositions of the mixed crystals, which separate from the various solutions, in the dry state; these results were obtained from

the analysis of the wet solid by allowing for the amounts of salt present in the adherent mother-liquor. Fig. 3 gives the gram-percentage of lead nitrate in the mixed crystals against the gram-percentage of lead nitrate in the total salt dissolved in the solution from which the crystals separate at 25°, whilst Fig. 4 gives the corresponding curve at 50°.

KNO_3–$Pb(NO_3)_2$–$Ba(NO_3)_2$–H_2O at 25°.

Solution.				Dry solid.			
KNO_3.	$Pb(NO_3)_2$.	$Ba(NO_3)_2$.	H_2O.	KNO_3.	$Pb(NO_3)_2$.	$Ba(NO_3)_2$.	Phases.
15·26	2·12	6·05	76·57	43·23	0·10	56·67	D.S.+ M.C.
17·39	11·44	3·40	67·77	41·98	0·43	57·59	,,
15·99	13·82	4·76	65·43	43·45	0·80	55·75	,,
16·01	21·25	4·33	58·41	43·51	1·70	54·79	,,
15·65	26·59	4·06	53·70	0·88	31·36	67·76	,,
17·87	35·90	2·46	43·77	23·10	14·95	61·95	,,
23·41	37·68	2·11	36·80	23·78	38·10	38·12	,,
25·75	34·65	1·16	38·44	69·45	4·42	26·13	D.S.+ M.C.+ KNO_3
25·74	32·63	1·92	39·71	91·23	1·36	7·41	D.S.+ KNO_3
26·78	23·26	1·76	48·20	92·31	0·61	7·08	,,
27·23	15·28	2·32	55·17	96·06	0·23	3·71	,,
27·69	9·85	1·87	60·59	92·13	0·10	7·77	,,
27·74	4·95	1·92	65·39	63·28	0·30	36·42	,,
25·22	40·46	0·72	33·60	45·44	51·86	2·70	KNO_3 + M.C.
25·00	39·84	1·18	33·98	2·11	28·02	69·87	,,
25·00	38·00	1·59	35·41	10·61	76·19	13·20	,,
24·91	37·48	1·80	35·81	94·90	1·31	3·79	,,

M.C. refers to $Pb(NO_3)_2$–$Ba(NO_3)_2$ mixed crystal.

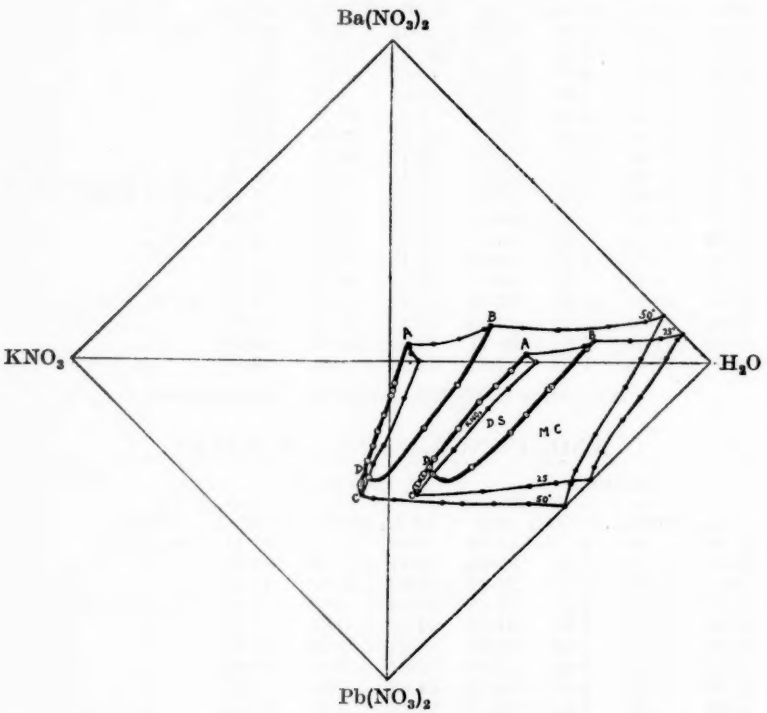
KNO_3–$Pb(NO_3)_2$–$Ba(NO_3)_2$–H_2O at 50°.

Solution.				Dry solid.			
KNO_3.	$Pb(NO_3)_2$.	$Ba(NO_3)_2$.	H_2O.	KNO_3.	$Pb(NO_3)_2$.	$Ba(NO_3)_2$.	Phases.
27·40	15·89	8·11	48·60	1·04	6·15	92·81	D.S.+ M.C.
28·28	27·00	5·68	39·04	9·41	11·94	78·65	,,
32·61	38·93	2·15	26·31	15·02	47·42	37·56	,,
35·48	33·62	2·01	28·89	91·53	1·02	7·45	D.S.+ KNO_3
36·91	29·22	2·24	31·63	92·65	0·00	7·35	,,
38·06	24·98	2·59	34·37	65·31	1·62	33·07	,,
39·43	19·96	2·85	37·76	57·61	0·94	41·45	,,
40·90	14·64	3·32	41·14	54·03	0·65	45·32	,,
41·39	13·01	3·44	42·16	71·12	0·44	28·44	,,
41·86	10·35	3·69	44·10	97·69	0·19	2·12	,,
33·25	40·88	1·02	24·85	53·25	43·15	3·60	KNO_3 + M.C.
33·41	40·19	1·51	24·89	34·54	35·58	29·88	,,
32·64	39·82	2·40	25·14	46·76	46·12	7·12	,,

The two isotherms in this quaternary system have been drawn from the above results by the method of Schreinemakers, as this was found to give the least confusing diagram, and are represented in Fig. 5. The points A, B, and C represent the composition of ternary liquids which are in equilibrium with two solid phases—potassium nitrate and double salt, double salt and lead nitrate, and potassium and lead nitrates, respectively—whilst the points on the

curves AD, BD, and CD give the composition of quaternary solutions in equilibrium with double salt and potassium nitrate, double salt and mixed crystal, and potassium nitrate and mixed crystal, respectively. The point D represents the composition of the quaternary isothermal invariant solution. The composition of the dry solid given in the above tables was obtained by calculating, from the analysis of the solutions, the amounts of the three nitrates dissolved in the water which was present in the wet solid and deducting

FIG. 5.



these from the total amounts found by the analysis of the dried residue.

An examination of the results given above for the quaternary system shows that when the two solid phases in equilibrium with saturated solution should consist only of potassium nitrate and double salt, there is also present a small amount of lead salt; the results are so consistent as to rule out the possibility of experimental error. The presence of lead has been confirmed by washing the wet solids with a little water and grinding the residue at 30—35° with a solution, containing roughly 25% of potassium nitrate and 2%

of barium nitrate, which dissolves lead nitrate very readily. The solid was then filtered off and ground up with a fresh portion of the solution; this process was repeated several times, but even after ten treatments the solid residue still contained an appreciable quantity of lead salt. These results indicate that lead nitrate in some form is separating as a mixed crystal either with potassium nitrate or else with the double salt. The most probable explanation is that the double salt $2KNO_3,Pb(NO_3)_2$, which has no stable existence alone under ordinary conditions, is separating out from solution as a mixed crystal with the barium double salt of similar formula. Other explanations are, of course, possible, but they seem to be less probable.

In order to obtain, if possible, further evidence for the existence of the double salt of lead and potassium nitrates, the results for the systems from which the potassium–barium double nitrate and mixed crystals of lead and barium nitrates separate were examined as follows. It was assumed as a first approximation that all the potassium nitrate in the solid phase was in the form of the double salt with barium nitrate, and so the amount of barium nitrate present as double salt was calculated; the residual barium nitrate was assumed to be present as mixed crystal with lead nitrate. In this way, the ratio of lead nitrate to barium nitrate in the mixed crystal was determined and compared with the ratio of these two salts in the quaternary solution. The results are given below.

25° $\frac{Pb(NO_3)_2}{Pb(NO_3)_2 + Ba(NO_3)_2}$ %.		50° $\frac{Pb(NO_3)_2}{Pb(NO_3)_2 + Ba(NO_3)_2}$ %.	
Solution.	Mixed crystal.	Solution.	Mixed crystal.
94·69	82·49	94·75	72·35
86·76	32·00	82·62	15·09
77·07	12·78	66·20	6·32
25·95	10·67		

These results have been plotted in Figs. 3 and 4 for 25° and 50° respectively for the purpose of comparison with the results for the ternary system. It is seen that for a given ratio of lead nitrate to barium nitrate in the solution the mixed crystal separating from the ternary solution contains relatively more lead than does that separating from the quaternary system; if a lead–potassium nitrate double salt had been present, then the reverse would have been expected. It is possible, however, that the presence of potassium nitrate in the solution alters the ratio of lead to barium in the mixed crystal, and so no definite conclusions can be drawn from the results.

Summary.

(1) The ternary systems KNO_3–$Ba(NO_3)_2$–H_2O and $Pb(NO_3)_2$–$Ba(NO_3)_2$–H_2O have been investigated at 25° and 50°.

(2) The quaternary system KNO_3–$Ba(NO_3)_2$–$Pb(NO_3)_2$–H_2O has been investigated at 25° and 50°.

(3) There is shown to be some evidence for the existence of a double salt, $2KNO_3,Pb(NO_3)_2$, in the form of a mixed crystal with the double salt $2KNO_3,Ba(NO_3)_2$.

UNIVERSITY COLLEGE, EXETER. [*Received, November 3rd,* 1925.]

CCCXCV.—*The Behaviour of Glucose and Certain Other Carbohydrates towards Dyestuffs and towards Potassium Ferricyanide in an Alkaline Medium.*

By EDMUND KNECHT and EVA HIBBERT.

ALTHOUGH we are well informed as to what changes take place in the dyestuff when indigo or some other dyestuff is reduced by glucose in presence of alkali, no attempts to elucidate the character of the oxidation of the glucose have hitherto been recorded. Many attempts have, however, been made to ascertain the character of the oxidation products formed by the action of Fehling's solution and of cupric hydroxide in presence of caustic alkali as well as of other inorganic oxidising agents in an alkaline medium, the results of which indicate that the reactions are of a complicated character. The most complete researches on this subject are those of Gaud (*Compt. rend.*, 1894, **119**, 604), who employed Fehling's solution as the oxidising agent and obtained formic, oxalic, tartronic, lactic, and glyceric acids, along with some catechol, and the elaborate work of Nef (*Annalen*, 1907, **357**, 214) who, using copper sulphate and a slight excess of caustic soda, obtained hexonic, trihydroxybutyric, glyceric, glycollic, formic, and carbonic acids. By means of red mercuric oxide and barium hydroxide, Herzfeld (*Annalen*, 1888, **245**, 32) obtained gluconic acid as the main product. By using sodium hypoiodite as the oxidising agent, Romijn (*Z. anal. Chem.*, 1897, **36**, 19) obtained this acid alone, and Willstätter and Schudel (*Ber.*, 1918, **51**, 780) showed that the reaction may serve for the estimation of glucose.

The authors have shown (*J. Soc. Dyers Col.*, 1925, **41**, 94) that when glucose is boiled with excess of methylene-blue in presence of caustic soda, oxidation takes place very rapidly, and to a definite degree (three atoms of oxygen to one mol. of glucose). Further work in this direction has now been carried out. Methylene-blue was not entirely suitable for the purpose on account of its great liability to undergo decomposition by the action of the alkali

(Bernthsen, *Annalen*, 1885, **230**, 73), so potassium indigotintetrasulphonate, which reacts in the same way as methylene-blue, is much more stable towards alkalis, and can be estimated volumetrically with rapidity and accuracy, was used for most of the oxidations given below. The amount of indigotin reduced was invariably equivalent to three atoms of oxygen per mol. of glucose, four atoms of oxygen per mol. of lævulose and, as might have been expected, $3\frac{1}{2}$ atoms of oxygen in the case of invert-sugar. Galactose and glucosamine hydrochloride behaved like glucose, each taking up three atoms of oxygen. Maltose was apparently hydrolysed, since the molecule ($C_{12}H_{22}O_{11} + H_2O$) reduced an amount of indigotin equivalent to six atoms of oxygen.

Thioindigodisulphonic acid (*Ber.*, 1907, **40**, 3821) gave with glucose and lævulose results identical with those obtained with potassium indigotintetrasulphonate.

Potassium ferricyanide can replace indigotin in the titration of glucose, lævulose, and glucosamine, giving identical results; the reaction is very rapid, being complete in 15 seconds. The extent of the oxidation was in the first instance determined by titrating the ferrocyanide in the cooled solution, acidified with sulphuric acid, with permanganate to the appearance of a pink colour. The result was corroborated by estimating the excess of ferricyanide by means of standard sodium hydrosulphite, with methylene-blue as indicator. Ultimately it was, however, preferred to estimate the excess ferricyanide by titration with titanous chloride in presence of a trace of ferric chloride, the disappearance of the blue colour indicating the end-point. There was a close agreement of the results in all three cases.

In view of the constancy of the results obtained with methylene-blue, potassium indigotintetrasulphonate, thioindigodisulphonic acid, and potassium ferricyanide, and the exact stoicheiometric character of the reactions, it was surmised that, in the case of glucose and galactose, the oxidation had resulted in the formation of hexane tetrahydroxy-dicarboxylic acids corresponding to saccharic and mucic acids, whilst in the case of lævulose, the oxidation would just suffice to produce a mono- and a di-carboxylic acid in equimolecular proportions. In spite of numerous attempts, it has, however, not been possible to identify any of the oxidation products. The difficulty lies mainly in the removal of the large quantity of colouring matter required to effect the oxidation; for instance, 1 g. of glucose requires more than 16 g. of potassium indigotintetrasulphonate, which will be present, after oxidation is complete, partly as such but mainly in the reduced condition. Also, through the action of the alkali, considerable isomerisation of

the oxidation products probably takes place, and these do not possess the uniformity of the product of oxidation in an acid medium.

If glucose, which is neutral to phenolphthalein, is converted into a dicarboxylic acid (or acids) during the reaction, the extent of such conversion should be measurable by titration, for the resulting acid would require two equivalents of caustic alkali for its neutralisation. On similar grounds, the acids resulting from the alkaline oxidation of lævulose should require three equivalents of alkali. It was obviously impossible to use dyestuffs as oxidants to test the validity of this reasoning. Pure potassium ferro- and ferri-cyanides are neutral to phenolphthalein, and the latter was employed as the oxidant in the experiments. In carrying out the estimations it had to be taken into consideration that potassium ferricyanide, in becoming reduced to ferrocyanide, takes up two molecules of potassium hydroxide for each atom of oxygen supplied. The results confirmed exactly the above reasoning.

It is known that, in the titration of glucose by means of Fehling's solution, the extent of the oxidation, as measured by the amount of copper reduced, is represented by rather less than $2\frac{1}{2}$ atoms of oxygen per molecule of glucose. On the other hand, it has been shown that by employing, in place of Fehling's solution, the solution of copper carbonate in potassium carbonate and bicarbonate advocated by Soldaini (*Gazzetta*, 1876, **6**, 322), the degree of oxidation is almost doubled (see also Ost, *Ber.*, 1890, **23**, 1035, 3003).* It was therefore considered possible that the use of an alkaline carbonate in the titration of glucose with indigotin might also give rise to a higher degree of oxidation. The results obtained, however, were in no way modified by substituting for the potassium hydroxide an amount of potassium carbonate and bicarbonate equivalent to that employed in the alkaline copper carbonate solution. In carrying out the titration, it is important that the substances be added in the sequence given. If the caustic potash is added to the boiling glucose solution before the indigotin, 30 seconds' boiling is sufficient to lower the result by 50% or more. This seems to be due to the conversion of some of the glucose into lactic acid (Nencki, *J. pr. Chem.*, 1881, **24**, 498). If the boiling is continued for 2 minutes, the amount of alkali neutralised corresponds exactly to the formation of two molecules of lactic acid. Lævulose behaves in this respect like glucose.

Neither lactic, saccharic, mucic, nor gluconic acid reduced

* No satisfactory explanation of this great difference in the behaviour of the two solutions has hitherto been advanced.

methylene-blue when boiled with this dyestuff in presence of caustic potash.

When kitone-blue *A*, (*p*) $SO_3Me{\cdot}C_6H_3(SO_3[o]){\cdot}C{<}\begin{matrix}C_6H_4{\cdot}NEt{\cdot}C_7H_7\\ C_6H_4{\cdot}NEt{\cdot}C_7H_7\end{matrix}$,

was substituted for methylene-blue or potassium indigotintetrasulphonate as oxidant, both glucose and lævulose took up exactly two atoms of oxygen per molecule. This would correspond to the formation of glycuronic acid from the first and of hydroxygluconic acid from the second of these carbohydrates. Superimposing an indigotin titration on the kitone-blue titration of glucose resulted in a further atom of oxygen being taken up. From its behaviour towards methylene-blue and towards indigotintetrasulphonic acid, it might have been expected that lævulose, after being oxidised with kitone-blue, would take up two more atoms of oxygen on superimposing a methylene-blue titration. Only one further atom of oxygen was taken up.

Rosinduline 2*B*, when employed as the oxidising agent, supplied only one atomic proportion of oxygen to glucose. By superimposing a methylene-blue titration, no further oxidation took place; and, although the oxidation product was not identified, this circumstance strengthens the opinion that the oxidation had resulted in the quantitative formation of gluconic acid.

Experimental.

In principle, all the titrations are carried out in the same way. A known weight of the carbohydrate is heated with a known volume of a standard solution of the oxidising dyestuff, which must be present in considerable excess, in a current of nitrogen. When the mixture boils, caustic potash is added, and the boiling continued for the time specified. The mixture is now at once acidified, and the excess of dyestuff titrated with titanous chloride in a current of carbon dioxide. The quantity of carbohydrate most suitable for a titration is 0·01—0·05 g., and the quantity of caustic potash required is about 0·5 g., or 5 c.c. of a 10% solution.

The following special points should be noted in carrying out the titrations.

Methylene-blue. A suitable strength of this dyestuff (working with a titanous chloride solution of which 1 c.c. = 0·002 g. Fe or thereabouts) is 10 g. of the medicinal product per litre. The time of boiling in presence of alkali should in no case exceed 5 seconds; beyond this limit, the methylene-blue loses strength through decomposition and the results become untrustworthy.

Potassium indigotintetrasulphonate. A suitable strength is 40 g.

of the crystallised dyestuff per litre. The procedure consists in adding to an aqueous solution of a definite weight of glucose excess of the standard indigotin solution. The mixture is boiled in a current of nitrogen, caustic soda is added, and the boiling continued for ½ minute. The mixture is then acidified with dilute sulphuric acid, excess of tartrate of soda added, and the hot solution titrated with titanous chloride until the blue colour disappears.

Ferricyanide. A suitable strength for a standard solution is 50 g. per litre. The quantity of caustic potash added should be more than sufficient to allow for the formation of ferrocyanide and for the neutralisation of the organic acids formed. The time of boiling is 15 seconds. The mixture is rapidly cooled in running water before being acidified with dilute sulphuric acid. The excess ferricyanide is then titrated with standard titanous chloride, as described. It is not necessary to employ either nitrogen or carbon dioxide.

Kitone-blue. A suitable strength is 10 g. per litre. Boiling for 30 seconds suffices to complete the oxidation, after which the solution is acidified with tartaric acid in slight excess before the excess of dyestuff is titrated with titanous chloride.

Rosinduline 2B. Strength and procedure as for kitone-blue. Rosinduline *G* also may be used for the purpose. *Crystal-scarlet* was not found suitable as an alkaline oxidising agent, the end-point not being sharp. Like the rosindulines, this dyestuff supplies one atom of oxygen to glucose.

Titration of Glycuronic Acid.—A solution of pure euxanthic acid (0·201 g.) in sulphuric acid (*d* 1·735) was diluted, boiled and filtered, and the separated euxanthone was washed so that the filtrate contained the whole of the glycuronic acid. The solution thus obtained reduced indigotin equivalent to 26·4 c.c. of $TiCl_3$ (1 c.c. $TiCl_3 = 0{\cdot}002001$ g. Fe), indicating that almost exactly one atom of oxygen had been used. Expressed as percentage of glycuronic acid in euxanthic acid, the result gives 45·5% as against 45·9% calculated for $C_{19}H_{16}O_{10} + H_2O$. Almost the same result was obtained in the osazone process: 0·035 g. of the same specimen of euxanthic acid was hydrolysed with sulphuric acid as before, and the resulting glycuronic acid converted into the osazone; this required 14·4 c.c. of $TiCl_3$ (1 c.c. = 0·001924 g. Fe) (Found: 45·7% calculated on the euxanthic acid employed).

Action of Sodium Hydroxide on Glucose and Lævulose.—An aqueous solution of 0·5045 g. of glucose was boiled with 25 c.c. of *N*-sodium hydroxide for 2 minutes, and the excess of alkali then titrated with *N*-sulphuric acid and phenolphthalein. The amount of caustic soda neutralised was 5·6 c.c., which is equal

to 44·4% on the weight of the glucose (calc. for *N*-NaOH, 44·5%).

0·5115 Gram of lævulose, similarly treated, required 5·7 c.c. of *N*-sodium hydroxide, which represents 44·4% on the weight of the lævulose. In another experiment the boiling with caustic soda was continued for 5 minutes; this did not affect the result.

Acidimetric Titration of the Oxidation Products of Glucose and Lævulose.—Glucose (0·5 g.) was oxidised with 7·5 g. of potassium ferricyanide and 50 c.c. of *N*-potassium hydroxide. Titration with *N*-sulphuric acid and phenolphthalein then showed that 1·24 g. of potassium hydroxide had been neutralised in the reaction. The amount required according to the equation is 1·245 g.

On similar treatment of 0·5 g. of lævulose, 1·45 g. of potassium hydroxide were neutralised (calc., 1·40 g.).

Indigotin Titration superimposed on Kitone-blue Titration.—0·02084 Gram of glucose required kitone-blue equivalent to 13·6 c.c. of $TiCl_3$ (1 c.c. = 0·001916 g. Fe), which (for 2 atoms of oxygen supplied) corresponds to 0·02094 g. of glucose or 100·4%. In the superimposed indigotin titration, an amount of indigotin equivalent to 6·9 c.c. of $TiCl_3$ was required, corresponding (for one additional atom of oxygen) to 0·02123 g. of glucose or 101·3%.

Sugar.	Oxidant.	Sugar taken (g.).	Titre of $TiCl_3$ (1 c.c. = $-\times 10^{-4}$ g. Fe).	$TiCl_3$ (c.c.).	Sugar found (g.).	% of sugar taken.
Glucose	M	0·03956	27·42	26·7	0·03922	99·15
,, ...	I	0·0400	18·38	40·5	0·03988	99·7
,, ...	Th	0·03733	19·23	36·2	0·037286	99·8
,, ...	F	0·02029	19·23	19·7	0·02032	99·8
,, ...	R	0·0400	19·98	12·4	0·03984	99·6
,, ...	K-b	0·0200	19·98	12·5	0·020075	100·4
Lævulose	M	0·04006	20·81	48·1	0·04023	100·4
,, ...	I	0·02023	19·15	26·2	0·02016	99·7
,, ...	Th	0·0400	19·23	51·5	0·03976	99·4
,, ...	F	0·0390	19·23	50·5	0·03898	99·9
,, ...	K-b	0·0200	19·98	26·2	0·03033	100·3
Sucrose (inv.)...	M	0·0291	15·72	42·5	0·02914	100·1
,, ...	I	0·0227	20·01	25·9	0·02261	99·6
,, ...	F	0·0227	20·01	26·0	0·02269	99·9
Galactose	M	0·0388	17·24	42·0	0·03879	99·8
,, ...	I	0·03304	18·45	33·4	0·03300	99·8
Arabinose	I	0·0400	20·66	42·4	0·03911	97·8
Glucosamine hydrochloride	I	0·05232	19·23	42·3	0·05219	99·7
Glucosamine hydrochloride	F	0·02505	17·49	22·2	0·02493	99·5
Glycuronic acid in euxanthic acid.....	I	0·2010	20·01	26·4	0·09150	45·5

M, methylene-blue; I, potassium indigotintetrasulphonate; Th, thio-indigodisulphonic acid; F, potassium ferricyanide; R, rosinduline; K-b kitone-blue.

Various amounts of glucose with potassium indigotintetrasulphonate as oxidising agent.

Glucose taken (g.).	C.c. of $TiCl_3$ used.	Glucose found (g.).	% of glucose taken.
0·052675	50·1	0·052505	99·7
0·04214	40·2	0·042129	99·9
0·02107	20·0	0·02096	99·5
0·010535	10·1	0·010585	100·4
0·0052675	5·0	0·00524	99·5

1 C.c. $TiCl_3$ = 0·001956 g. Fe.

Various amounts of glucose with potassium ferricyanide as oxidising agent.

0·0800	65·3	0·0798	99·8
0·0500	41·0	0·0500	100·05
0·0400	32·6	0·0399	99·7
0·0198	16·2	0·0198	100·0
0·0099	8·1	0·0099	100·0

1 C.c. $TiCl_3$ = 0·002272 g. Fe.

Summary.

1. It is shown that, in an alkaline medium, glucose, lævulose, and certain other carbohydrates are oxidised to a definite degree by methylene-blue and by potassium indigotintetrasulphonate. Glucose, glucosamine, and galactose take up, under the conditions, exactly three, and lævulose four, atomic proportions of oxygen. Potassium ferricyanide can replace the dyestuffs in these estimations.

2. When boiled for two minutes with excess of caustic soda in an atmosphere of nitrogen, both glucose and lævulose neutralise an amount of alkali corresponding exactly to the formation of two molecules of lactic acid.

3. When glucose is boiled with excess of potassium ferricyanide and caustic potash, the amount of alkali neutralised (over and above that required to form potassium ferrocyanide) represents exactly three equivalents of caustic potash. In the case of lævulose, the amount of caustic potash neutralised is approximately four equivalents.

4. Glycuronic acid can be estimated quantitatively by titration with potassium indigotintetrasulphonate. The volumetric osazone titration method may also be employed for the purpose.

5. In presence of caustic alkali, glucose is also oxidised quantitatively by kitone-blue and by rosinduline. In the former case, two, and in the latter, one atomic proportion of oxygen is supplied by these dyestuffs.

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CCCXCVI.—*The Salting-out Effect. The Influence of Electrolytes on the Solubility of Iodine in Water.*

By JOHN STANLEY CARTER.

THE fact that the solubility of non-electrolytes in water is lowered by addition of electrolytes has attracted considerable attention, and various empirical or semi-empirical equations have been put forward to express the relation between the change in the solubility and the concentration of the electrolyte. In most of the earlier work, the latter rarely exceeded one gram-equivalent per litre, and over this range the solubility lowering is approximately proportional to the concentration of the electrolyte. Experiments in which the electrolyte concentration was varied over a wider range show, however, that this proportionality by no means holds.

Measurements of the solubility of phenol in sodium sulphate solutions (Dawson, *J. Soc. Chem. Ind.*, 1920, **39**, 151T), of the solubility of ethyl ether in sodium chloride solutions (Thorne, J., 1921, **119**, 262) and of quinol and quinone in various salt solutions (Linderstrom-Lang, *Compt. rend. Trav. Lab. Carlsberg*, 1924, **15**, 4) show that, over a considerable concentration range, the influence of electrolytes on the solubility of non-electrolytes can be expressed by the exponential formula $s = s_0e^{-kc}$, first suggested by Setschenov (*Z. physikal. Chem.*, 1889, **4**, 117), where s_0 and s denote respectively the solubilities of the non-electrolyte in water and in a salt solution, the concentration of which, expressed in terms of the volume of the solution, is represented by c, and k is a constant characteristic of the dissolved electrolyte.

In the present investigation, the validity of the exponential formula has been tested by measurements of the solubility of iodine in aqueous solutions, the concentration of which ranged up to saturation at the temperature of observation. In previous measurements (Jakowkin, *Z. physikal. Chem.*, 1896, **20**, 19; Dawson, *ibid.*, 1906, **56**, 606), in which the salting-out effect was examined by determining the partition of iodine between carbon disulphide and aqueous salt solutions, the concentration of the electrolytes was varied only between comparatively narrow limits. The numbers thus obtained are consequently of little use for the present purpose.

The experimental data now recorded have reference to the effects produced by sodium nitrate, sulphate, and dihydrogen phosphate and by nitric and sulphuric acids. These are all readily soluble in water and do not react with iodine. The salts of weak acids are generally inadmissible on account of hydrolysis, and the halogen

salts are unsuitable because of the readiness with which they form perhalogen compounds. Various other salts had to be rejected on account of their oxidising properties, which introduce difficulties in the estimation of the iodine by means of thiosulphate. Measurements were also made with sodium chloride, allowance for the effect of perhalide formation being made in a manner which will be described later.

Experimental.

Iodine and the salts employed were purified by the customary methods. Since Bray (*J. Amer. Chem. Soc.*, 1910, **32**, 932) has shown that the hydrolysis of iodine is repressed in faintly acid solution, the values of p_H for the solutions of sodium nitrate, sulphate and chloride were adjusted to 5—5·5 by the addition of small quantities of the corresponding acids.

In the determinations of solubility, every precaution was taken to ensure complete saturation, efficient filtration, and to prevent loss of iodine by volatilisation. In the experiments with nitric and sulphuric acids, the dissolved iodine was extracted from a known weight of the saturated solution by repeated shaking with carbon tetrachloride; the latter was then freed from mineral acid by shaking with dilute aqueous sodium acetate. Freshly prepared 0·01*N*-sodium thiosulphate was used for the titrations. In order to obtain solutions of sufficiently high salt concentration, the first experiments (with sodium sulphate) were made at 35°, but subsequent measurements were made at 25° and 10°.

Determinations of the solubility of iodine in water with a slight acid reaction (p_H 5) gave the following results (millimoles per litre):

At 10°	0·835	0·837	
At 25°	1·319	1·321	1·322
At 35°	1·808	1·809	

The values at 25° agree with the value, 1·320, recorded by Bray (*loc. cit.*), but are lower than that, 1·334, given by Hartley and Campbell (J., 1908, **93**, 741), which is considered by Bray to be a little too high.

In Table I the solubilities experimentally determined are compared with those calculated from the exponential equation, which was put into logarithmic form,

$$\log s = \log s_0 - k'c \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (1)$$

the value of the constant k' being given by the slope of the line in the graph of log s–concentration.

In the application of this formula to the results obtained for the more concentrated solutions, the mode of expressing the concen-

tration of the dissolved electrolyte is a matter of great importance. The range of validity of the logarithmic formula is very much greater when the concentration of the electrolyte is referred to a fixed weight of water than it is when the concentration is expressed in terms of a fixed volume of solution. In the latter case, deviations appear when the concentration of the electrolyte reaches 2—3 gram-equivalents per litre, and the magnitude of these deviations increases continuously with the concentration of the dissolved salt.

For this reason, the concentrations of the electrolytes, c, represent the number of moles (equivalents in the case of sodium sulphate) per 1000 moles of water. The solubility of iodine is expressed in the same way, s' being the measured value and s the value calculated from equation (1). The values of s_0 at 25° and 35°, respectively, are 0·0238 and 0·0327. The ordinary weight percentage composition of the various solutions is given under "w%."

TABLE I.

Sodium Nitrate at 25°. $k' = 0{\cdot}00296$.

w %.	$s' \times 10^3$.	$s \times 10^3$.	w %.	$s' \times 10^3$.	$s \times 10^3$.	w %.	$s' \times 10^3$.	$s \times 10^3$.
5·89	22·2	21·8	25·67	14·5	14·5	39·83	9·11	9·16
11·10	20·2	19·9	29·75	12·5	12·9	44·16	7·53	7·60
15·31	18·5	18·4	35·43	10·8	10·8			

Sodium Nitrate at 35°. $k' = 0{\cdot}00243$.

1·98	32·7	32·3	15·89	26·8	26·2	50·1	10·0	9·94
3·48	32·0	31·4	29·06	20·1	20·1			
6·85	30·2	30·0	40·17	14·3	14·7			

Sodium Sulphate at 25°. $k' = 0{\cdot}0090$.

5·66	17·3	17·4	16·24	8·55	8·60	19·66	6·56	6·59
8·64	14·4	14·5						

Sodium Sulphate at 35°. $k' = 0{\cdot}0087$.

1·05	31·8	31·1	9·13	20·2	19·8	25·31	5·78	5·85
2·31	29·3	29·0	14·79	13·3	13·5	31·80	3·05	3·06
4·93	25·2	25·2	21·10	8·39	8·42	33·1	2·58	2·66

Sodium Dihydrogen Phosphate at 25°. $k' = 0{\cdot}0062$.

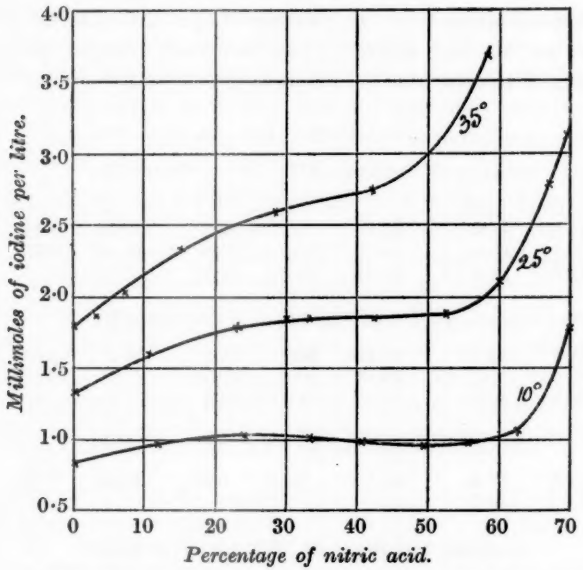
7·53	19·4	20·0	26·40	11·1	11·1	45·26	[1·8]	3·98
14·40	16·1	16·6	31·66	8·93	8·85			
20·64	13·5	13·7	41·06	[4·3]	5·35			

Comparison of the observed and the calculated solubilities of iodine shows that there is close agreement over the entire range of possible salt solutions in the case of sodium nitrate and sulphate; and also in the case of sodium dihydrogen phosphate, excepting the two most concentrated solutions, for which the measured solubilities are smaller than the calculated values. This divergence

suggests the operation of some factor other than that responsible for the normal salting-out effect. An explanation may possibly be found in the acid character of the electrolyte in this case, for, as will be seen later, the behaviour of nitric and sulphuric acids is quite different from that of the corresponding salts.

Iodine dissolved in a solution of sodium chloride exists in part as free iodine and partly in the form of a complex polyhalide. The influence of polyhalide formation is such that the solubility of iodine passes through a maximum when the concentration of the sodium chloride increases (Table II, column 2).

FIG. 1.



Solubility of iodine in aqueous solutions of nitric acid.

In order to obtain the value of k' in equation (1) for sodium chloride, it was assumed that the polyiodide equilibrium $NaCl + I_2 \rightleftarrows NaClI_2$ conforms to the requirements of the mass-law equation and that the variations in the value of the expression $[NaCl][I_2]/[NaClI_2] = a$ are due to the salting-out effect of the sodium chloride on the iodine. By plotting these values against the sodium chloride concentration and extrapolating to zero salt content, a limiting value of $a = 12{\cdot}0$ was obtained, and this was assumed to be the true value of the mass-law constant. In calculating the concentrations of free and combined iodine from this number, advantage was taken of the fact that the total salt concentration may be

substituted for [NaCl] in the mass-law equation without introducing any serious error.

TABLE II.

Sodium Chloride at 25°. $k' = 0{\cdot}00575$.

% NaCl.	Conc. of total dissolved iodine.	Conc. of combined iodine = [$NaClI_2$].	Conc. of free iodine = s'.	s.
4·52	0·04403	0·02405	0·0200	0·0197
7·43	0·05295	0·03560	0·0174	0·0172
14·14	0·06289	0·05085	0·0121	0·0122
20·31	0·06311	0·05475	0·00835	0·00843
23·15	0·06105	0·05405	0·00700	0·00698
25·95	0·05790	0·05210	0·00580	0·00571

The close agreement between the numbers in the last two columns of Table II affords clear evidence that the salting-out effect of sodium chloride is exactly similar to that of the other salts examined when due allowance is made for the disturbing influence of polyiodide formation.

Tables III and IV contain the data for solutions of nitric and sulphuric acid. As there is no simple relation between the solubility of the iodine and the concentration of the dissolved acid, the concentration of the iodine is expressed in millimoles per litre (b).

TABLE III.

Solubility of Iodine in Nitric Acid Solutions.

10°.		25°.		35°.	
% HNO_3.	b.	% HNO_3.	b.	% HNO_3.	b.
11·80	0·969	10·91	1·60	3·31	1·87
23·88	1·035	23·16	1·79	6·50	2·04
32·35	1·020	30·05	1·85	15·50	2·33
40·82	0·985	33·62	1·86	28·72	2·60
49·57	0·952	42·28	1·85	42·63	2·75
55·82	0·962	52·77	1·89	43·13	2·73
64·30	1·08	60·36	2·10	58·34	3·68
70·00	1·78	63·81	2·36		
		67·41	2·78		
		69·65	3·12		
		72·60	3·94		

TABLE IV.

Solubility of Iodine in Sulphuric Acid Solutions at 25°.

% H_2SO_4.	b.	Colour of sat. sol.	% H_2SO_4.	b.	Colour of sat. sol.
11·87	1·02	Brown.	40·42	0·545	Brown with pink tinge.
22·72	0·820	Brown.	59·53	0·380	Pink with brown tinge.
33·25	0·615	Brown.	72·04	0·270	Pink.
			87·37	0·200	Pink.

The somewhat complicated relations exhibited by the data for solutions of nitric acid are more clearly represented in the diagram.

The curve for 35° shows that the solubility increases continuously with the concentration of the acid, but the rate of increase diminishes markedly in the middle portion of the curve. The factors which give rise to this diminution have obviously a much greater influence at lower temperatures, in that the curve for 10° shows a maximum and a minimum. At 25°, the relations are intermediate in character; the form of the curve corresponds with the behaviour expected from the results at 10° and 35°. In connexion with these results, it may be noted that solutions containing more than 60% HNO_3, although brown when viewed in bulk, have a distinctly pink shade. In sulphuric acid solutions, the solubility of iodine decreases continuously as the concentration of the acid increases from 0 to 87%, but the data do not conform at all to the requirements of the logarithmic formula which expresses the salt effects. The colour of the solutions changes gradually from brown to pink.

There is apparently no connexion between the effects observed with nitric and sulphuric acid solutions and those obtained for neutral salt solutions. If the mineral acids exert any action which is comparable with that of the salts, it is more or less completely masked by other effects which play no part in the case of the neutral salts. It seems probable that the solvent power of nitric acid for iodine is in part responsible for the complicated behaviour exhibited by nitric acid solutions.

Recent measurements (Manchot, Jahrstorper, and Zepter, *Z. anorg. Chem.*, 1924, **141**, 45) of the solubility of nitrous oxide in aqueous solutions also have shown that the influence of the free mineral acids is totally different from that of the corresponding salts.

My thanks are due to Professor H. M. Dawson for suggesting the lines of this research and for his helpful criticism and advice.

UNIVERSITY OF LEEDS. [*Received, October 30th*, 1925.]

CCCXCVII.—*The Partial Pressures of Aqueous Ethyl Alcohol.*

By HILYARD JOHN EGLINTON DOBSON.

IN connexion with work now in progress, it became necessary to have accurate data for the partial vapour pressures of ethyl alcohol at 25°, for aqueous mixtures containing up to 90% of alcohol. The system is in itself of obvious importance, yet the existing data for these properties seem to be defective. Foote and Scholes

(*J. Amer. Chem. Soc.*, 1911, **33**, 1309) obtained figures for the aqueous partial pressure which exhibit a curious break in sequence; this they ascribe to experimental error. Wrewski, working at 39·7° (*Z. physikal. Chem.*, 1912, **81**, 1), obtained similar discontinuities in the same region between 20 and 40% alcohol. The system has therefore been newly studied by the method indicated below; the results prove to be free from the anomalies hitherto prevalent, and are believed to have considerable accuracy.

Method.—The partial pressures were measured by the dynamic or "bubbling" method. This method consists essentially in measuring the mass and composition of the mixed vapour which at 25° saturates a measured volume of a chemically inert gas, and

FIG. 1.

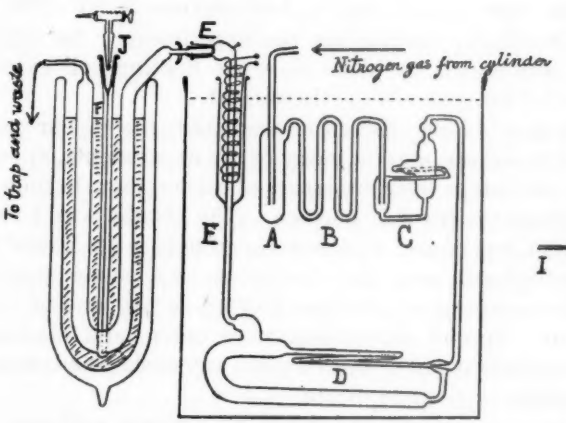


FIG. 1A.

thence calculating, with the aid of the simple gas laws, the partial pressures, or more accurately the vapour concentrations, of the two components alcohol and water. With some of the higher strengths of alcohol the mass and the composition of the vapour were measured simultaneously, but it was generally found more convenient to determine these separately for a given aqueous alcohol mixture. The determination of vapour composition is first described, and secondly the determination of the mass of vapour saturating a measured volume of gas.

Vapour Composition.—Nitrogen gas was saturated with the vapour of aqueous alcohol contained in a system of bubblers immersed in a thermostat electrically regulated at 25° ± 0·02°. The saturated vapour was then carried from the thermostat without condensation through an electrically heated tube, E (Fig. 1), to a U-tube immersed in a powerful refrigerant, and in this U-tube the vapour was quanti-

tatively condensed. The composition of the distillate was determined pyknometrically by the special means mentioned below.

Since for this purpose as much as 3 grams of liquid had to be distilled, it was essential to ensure that the change in composition of the final saturating bubbler was negligible. This was achieved by placing a slightly stronger alcohol mixture in the first bubbler, A, in which most of the evaporation occurred; the chilling due to latent heat was taken up in the long glass tube, B; whilst the remaining concentration changes were taken up by the second saturator, C, containing the same liquid as was in the final saturator, D. This was specially designed to remove all danger of spray being carried over from bursting bubbles; the absence of spray from this bubbler was proved in special experiments with highly coloured dyes.

The exposed tube, E, was covered with asbestos on which Nichrome wire was wound, and a temperature of 80—100° was maintained electrically throughout the experiment. An external glass sheath was sealed to E, so that the heating coil extended below the level of the water in the thermostat.

The U-tube proved very efficient in condensing the vapour quantitatively; and liquid air, used in many of the experiments, appeared to have little advantage over a mixture of carbon dioxide snow and ether as a refrigerant for this purpose. The U-tube was 2 feet in total length and was placed in a correspondingly large Dewar flask filled with refrigerant, and the distillation was made (generally over-night) in a current of nitrogen flowing at the rate of 1 to 3 litres per hour. Special precautions were taken, and mechanical indicators were devised which showed when any mishap had occurred. All determinations were in duplicate.

The method of sampling was as follows. When sufficient condensate had been obtained, the U-tube was removed from the Dewar flask, and the pyknometer (Fig. 1A) was fitted by the ground glass joint, J, to the sampling tube, F. When the condensate had thawed, and had been thoroughly shaken in the U-tube (to nullify fractionation), it was forced by air pressure into the bulb of the pyknometer to the mark H. The tap was then turned so as to close the bulb, and to connect the joint, J, to the side tube, I. A rubber cap was slipped over J, and the pipette was immersed in the thermostat at 25°. When equilibrium was attained, excess of alcohol was absorbed by spills of filter-paper, till the meniscus stood at the mark H. The pyknometer was now dried, and before weighing it the passage through the tap was washed out from I to J by sucking 30% alcohol through and drying the passage with a current of air.

In this way, weighings reproducible to 0·2 mg. were obtained, giving densities agreeing within less than 0·0001 unit. Densities

at 25° were used throughout for the estimation of percentage composition. This was read from the smooth curve obtained by plotting on a large scale the accurate data of Osborne and McKelvy (Landolt-Bornstein-Roth, " Tabellen," 1923 Ed., p. 448).

TABLE I.

The Vapour of Aqueous Alcohol.

Liquid. $d_4^{25°}$.	Weight % alcohol		Condensed vapour. $d_4^{25°}$.	Error of weight % figures.	Temp. of condensation of vapour.
	in liquid.	in vapour.			
0·98618	6·21	35·80	0·93990	0·03	−190°
0·97701	12·36	54·20	0·90045	0·04	−190
0·96572	20·51	66·17	0·87241	0·03	−190
0·95337	28·40	72·91	0·85634	0·01	− 80
0·94360	33·90	75·38	0·85038	0·04	−190
0·93285	39·32	77·10	0·84634	0·06	−190
0·90890	50·46	80·03	0·83903	0·02	− 80
0·89512	56·50	81·23	0·83614	0·04	−190
0·86068	71·09	84·40	0·82814	0·01	− 80
0·84392	78·07	86·20	0·82341	0·03	− 80
0·81337	90·12	91·90	0·80860	0·02	−190

The results of these determinations are in Table I, and each is the mean of two or more experiments. The maximum deviation from the mean figure for each concentration is expressed in the fifth column and shows the uncertainty in the percentage compositions. That these figures give a smooth vapour composition curve is shown in Fig. 2, in which these results are compared with the previous data of Foote and Scholes, which are here represented by crosses on a broken line.

Partial Pressures.—The apparatus used was a modification of that employed by Dobson and Masson (J., 1924, **125**, 673) in measuring the aqueous vapour pressure of hydrochloric acid. A current of nitrogen gas, saturated with the vapour of the aqueous alcohol at 25°, passed through a weighed bubbler containing about 50 g. of concentrated sulphuric acid, in which both the aqueous and the alcoholic vapours were quantitatively condensed (Masson and McEwan, *J. Soc. Chem. Ind.*, 1921, **40**, 29T). The device used for collecting the issuing gas at atmospheric pressures has been already described (Dobson, J., 1924, **125**, 1968); it materially increased the accuracy of the experiments, since it maintained in the saturator a constant total pressure, which was measured by a manometer. The importance of measuring this quantity has been emphasised by Berkeley (*Nature*, 1915, **95**, 54). Foote and Scholes were apparently able to neglect this through the arrangement of their apparatus, and on this account the method of calculation materially differs from theirs.

The volume of nitrogen, v, saturated at 25° with the vapour, is

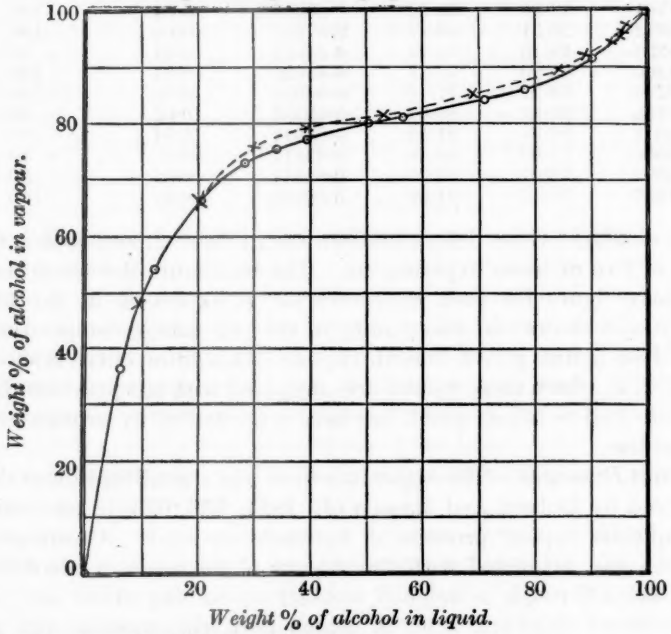
related by equation (1) to the volume, V, collected in the aspirator and measured at a temperature, $T°$ absolute, and a pressure, $B - h$, where B is the barometric height, and h the vapour pressure of water at the temperature of the aspirator, $T°$.

$$v = 298{\cdot}1\,V(B - h)/\{T(B_1 - p)\} \quad . \quad . \quad . \quad . \quad (1)$$

where B_1 is the total pressure in the saturator measured by the manometer, and $p = p_w + p_{alc}$, is the total vapour pressure of the mixture, which must be estimated by successive approximations.

FIG. 2.

The vapour composition of aqueous alcohol at 25°.



⊙ *Experimental points here determined.*
× *Found by Foote and Scholes* (1911, *loc. cit.*).
In no case were duplicate experiments sufficiently divergent to be shown by separate points on the scale of this figure.

The volume v is saturated at 25° by m grams of vapour, having a composition x% alcohol as given in Table I. Taking the molecular weights 18·02 and 46·06 for water and ethyl alcohol respectively, we obtain from the simple gas laws the following equations for the partial pressures :

$$p_w = \frac{3{\cdot}462\,mT(B_1 - p)}{V(B - h)} \times \frac{100 - x}{100} \quad . \quad . \quad . \quad (2)$$

$$p_{alc} = \frac{1{\cdot}354\,mT(B_1 - p)}{V(B - h)} \times \frac{x}{100} \quad . \quad . \quad . \quad . \quad (3)$$

Kendall (*J. Amer. Chem. Soc.*, 1920, **42**, 2481) has shown that saturated steam at 100° obeys van der Waals's equation when the constants a and b are deduced from the critical data. Calculation then shows that the deviation of saturated water vapour from the perfect gas laws amounts to only 0·03% at 25°. A similar calculation for saturated ethyl alcohol vapour at the same temperature shows that the gas laws hold within 0·1%. The accuracy of the equations is therefore as great as that of the experimental data.

The experimental figures are given in columns 2 to 7 of Table II. With the aid of equations 2 and 3, the partial pressures of aqueous and alcoholic vapour, p_w and p_{alc}, have been calculated and are given in columns 8 and 9.

TABLE II.

Experimental partial pressure results.

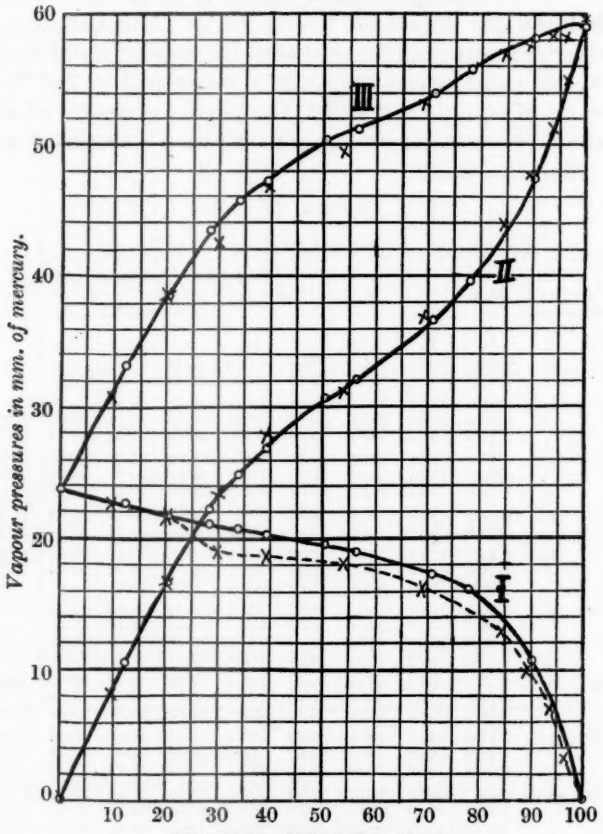
Wt. % alcohol.		Mass in grams.	Vol. litres.		Pressure in millimetres of mercury.						
							"Absolute."			"Relative."	
Liquid.	Vapour. x.	m.	V.	$T°$ abs.	$B-h$.	B_1.	p_w.	p_{alc}.	p_0.	p_w.	p_{alc}.
0	0	0·3449	15·10	293·9°	738·4	778·4	23·75	—	—	—	—
		0·4638	20·31	293·9	739·5	779·5	23·75	—	—	—	—
12·36	54·20	0·6107	12·24	292·5	742·2	764·4	22·80	10·55	—	—	—
		0·7888	16·00	293·2	740·3	763·2	22·60	10·46	23·80	22·55	10·44
		0·7454	15·10	293·9	738·4	762·1	22·71	10·51	23·75	22·71	10·51
20·51	66·17	0·9739	15·41	297·1	736·8	766·0	21·72	16·61	23·77	21·70	16·60
		1·0427	16·10	294·1	732·0	755·9	21·87	16·73	23·78	21·84	16·71
		1·0366	16·14	293·8	731·3	754·9	21·65	16·56	23·51	21·87	16·73
28·40	72·91	1·6580	20·30	285·8	749·4	768·3	21·17	22·29	23·74	21·18	22·30
		1·6316	20·33	286·7	735·8	763·3	21·11	22·22	23·71	21·15	22·26
33·90	75·38	1·4092	16·49	294·3	737·8	762·7	20·83	24·95	23·77	20·81	24·93
		1·3859	16·35	294·3	735·8	762·2	20·71	24·79	23·68	20·77	24·86
		1·2826	15·00	294·5	738·2	762·4	20·84	24·95	—	—	—
39·32	77·10	1·4590	16·37	296·7	732·2	754·1	20·24	26·65	23·45	20·50	26·99
		1·4367	16·10	297·5	731·9	754·7	20·34	26·79	—	—	—
		2·7841	31·10	294·7	741·9	761·1	20·13	26·50	23·45	20·39	26·84
		1·4955	16·15	292·0	746·5	763·0	20·55	27·07	23·73	20·56	27·09
50·46	80·03	2·0296	20·31	293·9	739·5	765·4	19·63	30·77	23·75	19·63	30·77
		2·0229	20·33	293·7	735·6	760·5	19·50	30·57	23·59	19·63	30·78
		2·0348	20·32	293·6	737·9	762·8	19·62	30·76	23·80	19·58	30·70
56·50	81·23	1·5886	15·02	290·5	747·2	760·7	18·96	32·09	23·65	19·04	32·22
		1·7458	16·36	289·0	749·7	763·3	19·04	32·22	23·86	18·95	32·07
		2·9705	28·26	292·4	732·0	748·9	19·04	32·22	—	—	—
71·09	84·40	2·3037	20·31	293·7	738·8	763·5	17·28	36·56	23·74	17·29	36·58
		2·3741	20·32	288·4	741·0	761·5	17·37	36·77	—	—	—
78·07	86·20	3·2033	26·18	291·3	745·5	764·5	16·19	39·56	23·63	16·27	39·76
		1·8569	15·30	292·7	728·2	745·4	16·08	39·28	—	—	—
90·12	91·90	1·9786	14·45	293·7	728·4	746·7	10·66	47·31	23·66	10·70	47·49
		2·1785	16·15	296·7	730·1	752·1	10·67	47·35	23·70	10·69	47·45
100	100	4·7172	29·70	292·3	746·0	759·3	—	59·01	—	—	—
Column 1)	(2)	(3)	(4)	(5)	(6)	(7)	(8)	(9)	(10)	(11)	(12)

As in the experiments of Dobson and Masson (*loc. cit.*), a simultaneous determination was made of the vapour pressure of pure water, figures being obtained for the mass of water saturating the same volume of gas at a total pressure, B_2, measured by a second manometer. Using an equation similar to equation 2 (in which x of course becomes zero), figures were obtained for p_0, the vapour

pressure of pure water, and these constitute column (10) of Table II. These figures provide not only a measure of the accuracy of the experiment, but taking the standard mean value $p_0 = 23{\cdot}75$ mm. at

FIG. 3.

The partial pressures of aqueous alcohol at 25°.



× *Found by Foote and Scholes,* 1911.
⊙ *Experimental points here determined.*
Curve I.—The partial pressure of aqueous vapour—p_w.
Curve II.—The partial pressure of alcohol vapour—p_{alc}.
Curve III.—The total vapour pressure—p.

25°, they yield an independent measure of the vapour pressures relative to that of water at the same temperature. The "*relative*" partial pressures so obtained are given in columns 11 and 12 of Table II.

In calculating the mean values of these experiments, both "*rela-*

tive " and " *absolute* " figures were considered to be of equal value, and these mean partial pressures, together with the total vapour pressures and the vapour compositions, are given in Table III.

The vapour pressure results have been plotted graphically in Fig. 3, in which they are compared with Foote and Scholes's results.

TABLE III.

Experimental Results.

Weight % alcohol		Vapour pressures in millimetres.			Weight % alcohol		Vapour pressures in millimetres.		
in liquid.	in vapour. x.	Aqueous.	Alcoholic.	Total.	in liquid.	in vapour. x.	Aqueous.	Alcoholic.	Total.
0	0	23·75	—	23·75	50·46	80·03	19·60	30·73	50·33
6·21	35·80	—	—	—	56·50	81·23	19·01	32·16	51·17
12·36	54·20	22·67	10·50	33·17	71·09	84·40	17·31	36·64	53·95
20·51	66·17	21·78	16·66	38·44	78·07	86·20	16·18	39·53	55·71
28·40	72·19	21·15	22·27	43·42	90·12	91·90	10·68	47·40	58·08
33·90	75·38	20·79	24·90	45·69	100	100	—	59·01	59·01
39·32	77·10	20·36	26·85	47·21					

Discussion.

It appears that these experimental results differ essentially from those of Foote and Scholes in the measurement of the composition of the vapour. For, when these authors' figures for partial pressures are recalculated, using vapour compositions interpolated from the present data instead of from their own, the resulting figures for the partial pressures fall in almost every case on the smooth curves of Fig. 3. Foote and Scholes (*loc. cit.*, p. 1317) used an analytical method in which the alcohol content of the vapours was determined by combustion over copper oxide, the percentage of water in the vapour being estimated by subtracting from the total water produced, 3/2 g.-mols. for each g.-mol. of carbon dioxide weighed. In spite of the analytical care displayed by these workers, it appears that inaccuracies were liable to occur, especially where the water content of the vapour was low.

The author wishes to express his indebtedness to Professor Irvine Masson for the interest he has taken in this work, and for much helpful criticism and advice.

THE UNIVERSITY, DURHAM. [*Received, October* 31*st*, 1925.]

CCCXCVIII.—*The Methylation of the Oximes of Benzil.**

By Oscar L. Brady and Hilda M. Perry.

The methyl ethers of the oximes of benzil were investigated by Auwers and Meyer (*Ber.*, 1888, **21**, 3510) and by Dittrich (*Ber.*, 1890, **23**, 3589), both of whom prepared them by the action of methyl iodide on the sodium salts. The former obtained from α-benzildioxime two compounds corresponding in composition to the methyl ethers α_1 (m. p. 165°) and α_2 (m. p. 109—110°), and from β-benzildioxime the ethers β_1 (m. p. 72°) and β_2 (m. p. 88°). Very little seems to be known of the constitution of these ethers, although Beilstein ("Organische Chemie," 3rd ed., Vol. III, 291, 293) assigns to α_2 and β_2 the structure of *OO*-dimethyl ethers, $C_{14}H_{10}(N{\cdot}O{\cdot}CH_3)_2$. Auwers and Meyer did not think that α_1 and β_1 were true dimethyl ethers of benzildioxime.

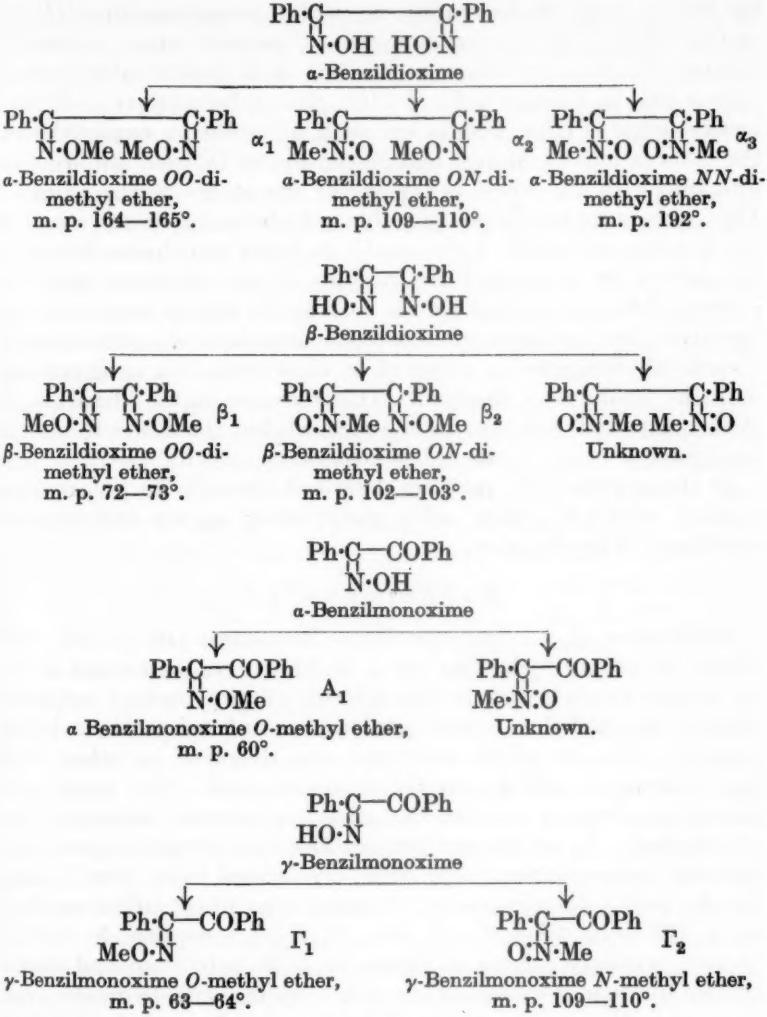
Dittrich obtained from α-benzilmonoxime a methyl ether A_1 (m. p. 62—63°) and from γ-benzilmonoxime an ether Γ_1 (m. p. 64—65°) which he regarded as *O*-ethers. Investigating the methyl ethers of the benzildioximes, he suggested that α_1 and α_2 were MeO·N:CPh·CPh:N·OMe and MeO·N:CPh·CPh·NMe, respectively.
O

From γ-benzildioxime by methylation he obtained the ether β_2, formed by isomeric change of the oxime during the reaction. On the other hand, Beilstein (*op. cit.*, 4th ed., Vol. VII, 760, 762), while accepting Dittrich's view of the constitutions of α_1 and β_1 as the result of a private communication from Auwers, assigns to α_2 and β_2 the constitutions CR(:NMeO)·CR(:NMeO).

The whole problem has now been reinvestigated, methyl sulphate being used as the methylating agent. The constitutions of the ethers have been established by heating them with hydriodic acid and determining the methyl iodide obtained from the *O*-ethers and detecting the methylamine from the *N*-ethers by Valton's method (this vol., p. 40).

On the Hantzsch-Werner theory, α-benzildioxime should give three methyl ethers, β-benzildioxime three, α-benzilmonoxime two, and γ-benzilmonoxime two. Of these ten, eight have now been characterised. The results are summarised as follows:

* The usual configurations are adopted for the oximes, and not those suggested by Meisenheimer (*Ber.*, 1921, **54**, 3206; 1924, **57**, 276, 282, 289).



γ-Benzildioxime on methylation gave an oil from which were isolated γ-benzilmonoxime *O*-methyl ether and benzil; the former was probably formed by the hydrolysis of an *ON*-dimethyl ether, and the latter from an *NN*-dimethyl ether, as the *N*-methyl compounds are hydrolysed with unusual ease.

On boiling with concentrated hydrochloric acid, α-benzildioxime *NN*-dimethyl ether gives benzil and α-benzildioxime *ON*-dimethyl ether gives γ-benzilmonoxime *O*-methyl ether, probably through α-benzilmonoxime *O*-methyl ether, the latter being converted into

the former under these conditions; whilst β-benzildioxime *ON*-dimethyl ether gives γ-benzilmonoxime *O*-methyl ether. α-Benzildioxime *OO*-dimethyl ether, on heating with concentrated hydrochloric acid in a sealed tube at 110°, gives β-benzildioxime *OO*-dimethyl ether. These results are such as would be expected and the observations of Auwers and Meyer and of Dittrich are brought into line with the usual behaviour of the ethers of the oximes: The *O*-ethers are exceptionally stable to hydrolysing agents, whereas the *N*-ethers are readily hydrolysed; the latter form hydrochlorides, the former do not; and the β-forms of the dioximes and the γ-forms of the monoximes are the most stable at high temperatures. Moreover, the formation of *O*-methylhydroxylamine, ammonia and *N*-methylhydroxylamine observed by these workers is in agreement with the results now obtained. The confusion in the literature of these compounds has thus been abolished, but the desire to obtain the complete series of ethers has been disappointed.

In the experimental part are described attempts to prepare the missing ethers by using other methylating agents and various conditions of methylation.

Experimental.*

Methylation of γ-Benzilmonoxime.—The oxime (10 g.) was dissolved in sodium hydroxide (10 g. in 120 c.c. of water and 5 c.c. of methyl alcohol) and to the filtered solution methyl sulphate (18 g.) was added in small portions, rise of temperature being avoided. The oil which separated was dissolved in ether, and light petroleum added; an oil then separated. The whole was placed in a freezing mixture and after five minutes' scratching the oil solidified. In subsequent preparations, rapid crystallisation was induced by inoculation. The solid, crystallised twice from boiling ligroin, gave *γ-benzilmonoxime* **N-*methyl ether*** in colourless needles, m. p. 109—110° (Found: N, 5·9. $C_{15}H_{13}O_2N$ requires N, 5·9%). It was sparingly soluble in ligroin or light petroleum and easily soluble in ether, benzene, or alcohol. Boiling with hydriodic acid gave no methyl iodide, but methylamine was detected by decolorising the solution with sulphur dioxide, making it alkaline with sodium hydroxide, and distilling into alcoholic 2 : 4-dinitrochlorobenzene, when 2 : 4-dinitromethylaniline was obtained (Valton, *loc. cit.*).

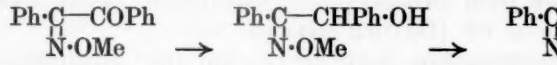
The ether–light petroleum mixture (above) was evaporated at room temperature, the residual oil dissolved in the minimum of

* It is important that all ethereal extracts should be dried before further treatment and that only anhydrous sodium sulphate should be used for this purpose.

ether, and light petroleum added, whereby a further quantity of the *N*-ether was precipitated. The filtrate on evaporation yielded an oil which solidified on treatment with a few drops of alcohol and scratching; this having been pressed on a porous tile and crystallised twice from alcohol, γ-benzilmonoxime *O*-methyl ether was obtained, m. p. 63° (Dittrich gives 64—65°).

Methoxyl determinations made to confirm the constitution of this compound gave consistently low results in presence or absence of acetic anhydride (MeO, 7·9, 8·6, 7·9. Calc., 1MeO, 13·0%). As the compound is somewhat readily volatile at 100°, a determination was carried out very slowly by heating first for an hour at 100° with the stream of carbon dioxide stopped and then at 135—140° as usual, but the result was worse (MeO, 7·4%). The heating with hydriodic acid was then carried out in a sealed tube, but a low result was again obtained (MeO, 8·2%). The compound was apparently pure, it consisted of well-formed, transparent crystals which seemed homogeneous under the microscope and remained unchanged in m. p. after crystallisation from various solvents. Dittrich obtained satisfactory analytical figures for carbon and hydrogen, and these have been confirmed (Found: C, 75·5; H, 5·5; N, 5·9. Calc., C, 75·3; H, 5·4; N, 5·9%). In view of the possibility that the substance might contain the isomeric *N*-ether the hydriodic acid solution from the methoxyl determination was examined by Valton's method (*loc. cit.*), but methylamine was not detected. Since the substance should contain some 30% of the *N*-ether to account for the low methoxyl value, and more than 0·3 g. of it was employed in the methoxyl determination, the amount of methylamine which would have been formed corresponds to 0·03 g. of methylamine hydrochloride; Valton's method will detect 0·005 g. of this compound. Moreover, no difficulty was experienced in detecting a similar amount of methylamine formed in the methoxyl determinations of the *ON*-dimethyl ethers of benzildioxime. Now γ-benzilmonoxime *O*-methyl ether is the stable isomeride, α-benzilmonoxime *O*-methyl ether passing into it on heating at 100° with concentrated hydrochloric acid. It will therefore be the first product formed when α-benzilmonoxime *O*-methyl ether and α- and β-benzildioxime *ON*-dimethyl ethers are heated with hydriodic acid (since the *N*-methylhydroxylamino-group is very easily eliminated in the last two cases); it is noteworthy that in these cases also similar low methoxyl values were obtained. If the *O*-methylhydroxylamino-groups are removed one at a time from the benzildioxime *OO*-dimethyl ethers, γ-benzilmonoxime *O*-methyl ether will be formed, and this probably accounts for the low but better methoxyl values obtained with these compounds.

If Meisenheimer's configuration (*loc. cit.*) be adopted, a possible explanation can be suggested involving reduction of the carbonyl group and ring formation by elimination of water from the resulting CH·OH and the methyl group. This point is being investigated.



Fortunately, in spite of this difficulty, the methoxyl determinations leave no doubt of the constitutions of the different ethers.

Methylation of α-Benzilmonoxime.—α-Benzilmonoxime was methylated in a similar manner as the γ-compound, and the oil which separated was removed with ether. Part of the extract on evaporation gave an oil which solidified on scratching (m. p. 54—58°); to the rest light petroleum was added until a faint turbidity was produced, and the solution left in a freezing mixture for 10 minutes, when some crystals separated (m. p. 54—58°). The mother-liquor was evaporated at room temperature; an oil was then obtained which solidified on scratching (m. p. 56—59°). No lowering of melting point occurred on mixing the various fractions, so if the second methyl derivative is formed the amount must be very small. Two crystallisations from methyl alcohol gave α-benzilmonoxime *O*-methyl ether, m. p. 58—59° (Found : MeO, 8·7, 8·5. Calc., 1MeO, 13·0%). Further search was made for the *N*-ether by distilling the mother-liquor from the first crystallisation in steam to remove the *O*-ether and extracting the residue with ether, but only a very small quantity of a red, uncrystallisable oil was obtained.

α-Benzilmonoxime *O*-methyl ether was boiled for 30 minutes under reflux with concentrated hydrochloric acid. The γ-benzilmonoxime *O*-methyl ether obtained on diluting the solution and extracting with ether was identified by the method of mixed melting points.

Preparation of α-Benzildioxime.—This oxime is best prepared by dissolving sodium hydroxide (80 g.) in water (500 c.c.) and adding, with cooling, a solution of hydroxylamine hydrochloride (40 g. in 100 c.c. of water) followed by finely powdered benzil (50 g.) and alcohol (25 c.c.). After 3 days, the small amount of unchanged benzil was filtered off and the oxime precipitated with carbon dioxide and extracted three times with boiling alcohol, in which the α-dioxime is almost insoluble. The residue melted at 230° and was considered sufficiently pure.

Methylation of α-Benzildioxime.—The oxime (10 g.) was dissolved in sodium hydroxide (30 g. in 200 c.c. of water) with the addition of a little methyl alcohol (5 c.c.). To the filtered solution, methyl

sulphate (42 g.) was added in small portions with shaking and cooling. An oil separated which slowly became pasty; this was collected and treated with a small quantity of ether, when a solid remained undissolved, m. p. 162°. Two crystallisations from alcohol gave a fine, crystalline compound, m. p. 165—166°; further crystallisation from alcohol did not raise the melting point. In a Zeisel estimation, silver iodide was produced in amount corresponding to 6·2% of OEt (Half a molecule of alcohol of crystallisation requires OEt, 7·7%); but the production of silver iodide may be due to contamination with *O*-methyl ether. The substance on crystallising three times from benzene gave large, colourless crystals, m. p. 185° (Found: N, 9·4; loss at 100°, 12·7. $C_{16}H_{16}O_2N_2,\frac{1}{2}C_6H_6$ requires N, 9·1; loss, 12·7%). On heating for 3 hours at 100°, the crystals became opaque and *α-benzildioxime* NN-*dimethyl ether* was obtained, m. p. 192° (decomp.) (Found: N, 10·5. $C_{16}H_{16}O_2N_2$ requires N, 10·4%). Neither of these compounds gave any alkyl iodide on heating with hydriodic acid. The association of solvent of crystallisation was not unexpected in view of the general tendency of the *N*-ethers of the aldoximes to separate with water of crystallisation. The *NN*-dimethyl ether is sparingly soluble in all ordinary solvents; it dissolves in concentrated hydrochloric acid in the cold and on boiling the solution benzil is formed.

The alkaline solution from the methylation was extracted with ether, and the extract added to the ether washings obtained in the preparation of the above compound. After removal of the solvent at room temperature an oil containing crystals of the *NN*-dimethyl compound was obtained. The oil was decanted off, the crystals were washed with a little alcohol, and the washings added to the oil. The solution so obtained was evaporated somewhat and concentrated hydrochloric acid added drop by drop until the whole consisted of a pasty mass, which was sucked as dry as possible. The hydrochloride was washed several times with concentrated hydrochloric acid and finally with warm ether, the ether washings being retained (A). The solid was decomposed with concentrated aqueous ammonia; a pasty mass was then formed which slowly solidified. Crystallised three times from light petroleum, it gave α-benzildioxime *NO*-dimethyl ether, m. p. 109°. This is apparently the compound, m. p. 109—110°, described by Auwers and Meyer (*loc. cit.*) (Found: MeO, 9·0, 9·4. Calc., 1MeO, 11·6%). Methylamine was detected in the hydriodic acid after the methoxyl determination.

α-Benzildioxime *NO*-dimethyl ether was boiled with concentrated hydrochloric acid for 30 minutes, and the mixture was diluted, and extracted with ether. Removal of the solvent gave an oil

from which crystals separated. After two crystallisations from alcohol, these proved to be γ-benzilmonoxime *O*-methyl ether, the :N(CH$_3$):O group having been removed and the *O*-ether of the α-monoxime converted into that of the γ-monoxime, a change which has been shown to occur under the conditions of the experiment.

The ether washings from the hydrochloride (A) were evaporated and the residue was distilled in steam. The small amount of oil which volatilised partly solidified on keeping, and the solid on crystallisation from dilute alcohol gave α-benzilmonoxime *O*-methyl ether, formed probably by the hydrolysis of the *NO*-dimethyl ether; no *OO*-dimethyl ether could be isolated and little if any of this compound appears to be formed under these conditions of methylation.

Auwers and Meyer apparently obtained the *OO*-dimethyl ether by the action of methyl iodide on the sodium salt of the oxime, but some doubt existed whether their compound, m. p. 165°, was actually the *OO*-dimethyl ether or the *NN*-dimethyl ether containing alcohol of crystallisation (m. p. 165°). A methylation with methyl iodide was carried out, a simpler technique than that of Auwers and Meyer being used; α-benzildioxime *OO*-dimethyl ether, m. p. 161°, and α-benzildioxime *NO*-dimethyl ether were obtained, but no *NN*-dimethyl ether.

A better method of obtaining α-benzildioxime *OO*-dimethyl ether consisted in mixing α-benzildioxime (2 g.) with dry silver oxide (2 g.) and methyl iodide (2·3 g.), diluting with dry ether, and heating under reflux for 2 hours. The mixture was filtered and the residue extracted twice with hot ether; on cooling, a solid separated from the filtrate. The solvent was evaporated at room temperature, leaving a solid and a small quantity of oil. The solid was crystallised three times from acetone and the α-benzildioxime *OO*-dimethyl ether described by Auwers and Meyer was thus obtained, m. p. 163—164° (Found: MeO, 18·8. Calc., 2MeO, 23·1%). This was identical with the somewhat less pure product (m. p. 161°) obtained above. The hydriodic acid solution from the methoxyl determination gave no methylamine when tested by the method described above.

Heated in a sealed tube with concentrated hydrochloric acid for 10 hours, α-benzildioxime *OO*-dimethyl either gave an oil; this solidified on scratching and after crystallising from alcohol was identified as β-benzildioxime *OO*-dimethyl ether. The observation of Auwers and Meyer was thus confirmed.

Preparation of β-*Benzildioxime.*—A much more satisfactory method of preparing β-benzildioxime than that described in the literature consists in dissolving α-benzildioxime in the minimum of freshly distilled boiling aniline; on cooling, β-benzildioxime con-

taining aniline of crystallisation separates. The crystals are sucked as dry as possible, washed with dilute hydrochloric acid, which removes the aniline of crystallisation, then with water, and crystallised twice from alcohol, when the pure β-dioxime is obtained.

Methylation of β-*Benzildioxime.*—β-Benzildioxime was methylated with methyl sulphate in a similar manner as the α-compound, and the oil obtained was extracted with as little ether as possible. The extract was washed several times with 0·2*N*-hydrochloric acid (to remove a trace of a basic compound which is simultaneously formed), dried, and saturated with dry hydrogen chloride; an oily hydrochloride then separated. The ether was decanted and light petroleum added. The additional hydrochloride thus obtained was added to the previous material and the whole was washed twice with small quantities of ether; the washings were added to the main bulk of the ether solution (B). The hydrochloride was decomposed with concentrated aqueous ammonia. The oil thus obtained was washed with water by decantation and left in an evacuated desiccator over solid sodium hydroxide. It slowly became very viscous, and after treatment with ligroin and 10 minutes' scratching it became pasty and finally solid (m. p. 83—89°). The ligroin washings, when allowed partly to evaporate at room temperature, deposited crystals (m. p. 88—90°). The solid (m. p. 83—89°) was heated with ligroin until it was on the point of melting, and the solution was then decanted and inoculated with a crystal of the above solid (m. p. 88—90°). This treatment was repeated with the residual semi-solid material until only a small quantity of dark oil remained. The extracts deposited an oil which solidified on keeping over-night. Fine needles projected from the solidified oil, and these melted at 90—92° and seemed to be identical with the compound, m. p. 88—89°, described by Auwers and Meyer. On keeping for some time, however, they became opaque and then melted at 102—103°. The solidified oil on crystallisation from ligroin gave the same product, m. p. 102—103°, which was β-benzildioxime *NO*-dimethyl ether (Found: MeO, 10·3. Calc., 1MeO, 11·6%). Methylamine was detected as before in the hydriodic acid from the methoxyl determination. When β-benzildioxime *NO*-dimethyl ether was heated with concentrated hydrochloric acid for ½ hour under reflux, and the mixture was cooled, diluted, and extracted with chloroform, an oil was obtained which partly solidified on cooling in ice and scratching. The solid, after purification, was found to be γ-benzilmonoxime *O*-methyl ether.

The ether–light petroleum solution (B) was evaporated at room temperature, and the solid obtained, after being freed from oil, was crystallised four times from alcohol; β-benzildioxime

OO-di-methyl ether was thus obtained, m. p. 72—73° (Found: MeO, 21·4. Calc., 2MeO, 23·1%). No methylamine was detected in the hydriodic acid residues. Methylation with methyl iodide and sodium methoxide as described by Auwers and Meyer gave the *NO*-dimethyl ether and the *OO*-dimethyl ether as above.

Methylation of γ-Benzildioxime.—The γ-dioxime was suspended in sodium hydroxide (15 g. in 100 c.c.), and methyl alcohol (5 c.c.) added, followed by methyl sulphate (21 g.) in small portions with cooling. The oil which separated was removed with ether, and the extract was washed with 0·2*N*-hydrochloric acid and treated with excess of light petroleum, which precipitated an oil (C). The mother-liquor was evaporated, the oil taken up with a little ether, and light petroleum again added; an oil (D) was precipitated. On decanting the solution and evaporating, an oil was obtained which solidified on keeping in an evacuated desiccator for some days. This solid, after crystallising twice from methyl alcohol, was found to be γ-benzilmonoxime *O*-methyl ether. The oil (C), on keeping in an evacuated desiccator for some time, partly solidified. It was then pressed on a porous tile, and the yellow solid crystallised from ligroin and from acetone and water, when benzil was obtained. The oil (D), on keeping, deposited crystals of γ-benzilmonoxime *O*-methyl ether, but all attempts to obtain a solid from the remaining oil were unsuccessful. The formation of benzil and γ-benzilmonoxime *O*-methyl ether suggests that *NN*- and *NO*-dimethyl ethers of γ-benzildioxime are formed, but are very readily hydrolysed. γ-Benzildioxime was boiled in ether with methyl iodide and dry silver oxide, and the solution was extracted with 2*N*-sodium hydroxide to remove unchanged oxime and evaporated. On keeping, the oil obtained deposited a few crystals (m. p. 145—157°), insufficient for further purification. All attempts to obtain a solid from the rest of the oil were unsuccessful.

Attempts to Prepare α-Benzilmonoxime N-*Methyl Ether and* β-*Benzildioxime* NN-*Dimethyl Ether.*—α-Benzilmonoxime was treated with methyl sulphate and with methyl iodide without other addition and also in ether with diazomethane. The dry sodium salt of α-benzilmonoxime was boiled with ether and methyl iodide, and benzil was treated with β-methylhydroxylamine under various conditions. None of these methods met with success. Attempts were also made to methylate β-benzildioxime with methyl sulphate and with methyl iodide without other addition, and in dry acetone solution, but no change was observed.

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CCCXCIX.—*Studies of Dynamic Isomerism. Part XX. Amphoteric Solvents as Catalysts for the Mutarotation of the Sugars.*

By Thomas Martin Lowry and Irvine John Faulkner.

1. In the preceding paper of this series (this vol., p. 1385), evidence was adduced to show that the mutarotation of the sugars is not due to a mere spontaneous tautomeric change, involving only the molecules of the sugar itself, but to a molecular rearrangement in

Fig. 1.

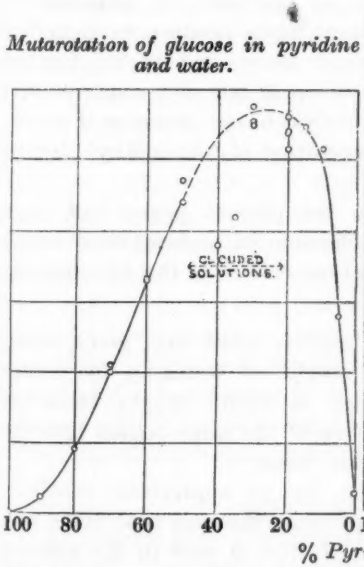
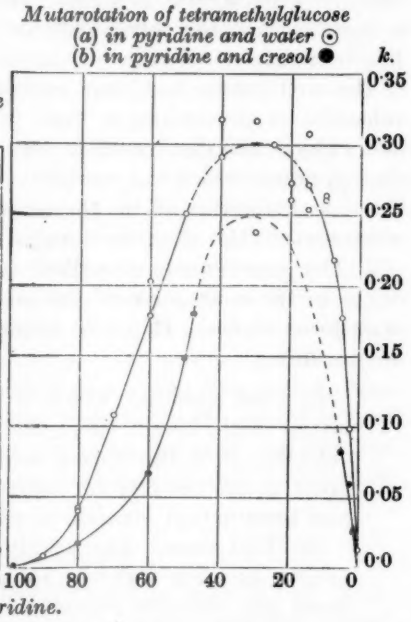


Fig. 2.



which other constituents of the solution also play an essential part. Of the constituents which interact catalytically with the sugar to bring about this rearrangement, water is the most important, since it was already obvious in 1904, from Irvine's work on the methylated sugars, that the mutarotation is retarded enormously, and in some cases may be almost stopped, by working in non-aqueous solvents. The opinion was therefore expressed (J., 85, 1566) that all the data then available could be interpreted by attributing the mutarotation to a process of "hydrocatalysis" of the sugar.

At that time, only one assertion could be made in reference to

the mechanism of this hydrocatalysis, namely, that, since glucose hydrate exhibits just the same mutarotation as glucose itself, the change of structure which causes the changes of rotatory power could not take place during the initial hydration of the sugar, but must occur at some subsequent stage, *e.g.*, by a molecular rearrangement or isomeric change in the hydrated sugar. A further consideration of the mechanism of mutarotation (this vol., p. 1371), especially in comparison with the mechanism of hydrolysis, led, however, to a much more definite suggestion, namely, that water probably acted as a catalyst for mutarotation in virtue of the fact that it possesses both acidic and basic properties, and that, in general, the essential condition for the mutarotation of a sugar is that the solvent should possess amphoteric properties. This conclusion has the advantage of providing an explanation of the well-known fact that acids and bases produce even higher velocities of mutarotation than water alone, and of the further fact (which was discovered in the course of our own experiments) that pyridine, which is a powerful catalyst in the presence of water, is not a catalyst at all for the mutarotation of tetramethyl glucose when used in the absence of water.

2. The experiments described in the present paper had their origin in the conception of the mechanism of mutarotation which is outlined above. The most important results of the experiments are to show:

(i) That pyridine, which is inactive when dry, gives, when mixed with about twice its weight of water, a maximum velocity of mutarotation which is about twenty times as great as the velocity for solutions of the same sugars (glucose and tetramethyl glucose) in pure water.

(ii) That cresol, like pyridine, has no appreciable catalytic properties when water is not present, showing that acids and bases may alike be rendered ineffective if used in the absence of water.

(iii) That mixtures of cresol and pyridine, each sufficiently dry to give only a negligible velocity of mutarotation, when mixed in the proportion of about 2 parts of cresol to 1 part of pyridine, are again about *twenty* times as active as water in promoting the mutarotation of tetramethyl glucose.

It is, of course, possible to argue that *perfectly* dry pyridine and *perfectly* dry cresol would be incapable of producing mutarotation; but this criticism, even if it could be vindicated by experiments on the effect of extreme drying, would not affect the present discussion, since it is clear that a mixture of pyridine

and cresol is able to do what neither solvent can do by itself, namely, to give a velocity of mutarotation which is far greater than in a solvent containing 100% of water. In other words, if a trace of water is essential (as it may be even in order to enable the acid and base to interact to form an unstable salt),* the intense activity of the mixed solvent is due to its pronounced amphoteric character, and not to a direct catalytic action upon the sugar of any minute trace of water which it may contain.

3. It is interesting to notice the theoretical conclusions which follow from the experimental facts thus established, namely, (i) that (just as in the case of nitrocamphor) it is impossible for a proton to wander directly from one position to another within the molecule of the sugar, and (ii) that in order to effect this transfer, it is necessary to provide a medium into which a proton can escape from the sugar, and from which a proton can be provided to replace the proton thus lost by the sugar.

These conclusions are supported by the fact that the only substances which are now known to act as catalysts for the mutarotation of the sugars are those which possess either acidic or basic properties, or both. Oxygenated solvents such as acetone and ethyl acetate, even when used in presence of water, retard rather than accelerate the mutarotation; and even their "polar" character and relatively high dielectric constants do not enable them to develop any catalytic activity. The mechanism of mutarotation suggested above, which involves an interchange of protons between the sugar and the medium (just as in the interaction of an acid and a base) appears therefore to be the only one which is in accord with the experimental facts, and no alternative mechanism is yet known which can replace it.

Experimental.

4. The *sugars* were the same samples as those used in Part XIX. The *solvents* used were as follows: (i) Air-free distilled water. (ii) *Pyridine* (B.D.H. "Extra Pure") shaken twice with quicklime for 24 hours and distilled, twice shaken with barium oxide and twice fractionated, giving about 800 c.c. boiling from 114·8° to 115·2° (corr.) from about 1 litre. The sample gave a residual velocity of mutarotation of tetramethyl glucose not greater than 0·0004 in minute-units. (iii) *o-Cresol* (B.D.H., "for cineol-determinations") from a sealed flask was distilled immediately before use; when liquefied by the addition of a little benzene, and used

* The melting-point curve for pyridine (m. p. −41°) and *o*-cresol (m. p. 30°) rises to a maximum at +1°, in an equimolecular mixture of the acid and base (Bramley, J., 1916, **109**, 476).

as a solvent for tetramethyl glucose, it gave an arrest of mutarotation during a period of 6 hours, followed by a slow change with a velocity coefficient of about 0·0005. m-*Cresol* (B.D.H., specially prepared) was redistilled and gave a velocity coefficient of 0·0003 only.

5. *Mutarotation-curves* were plotted as follows: One gram of sugar was weighed out in a 20 c.c. flask, and the mixed solvent, previously made up by weight in another vessel, was added at zero time. The solution was transferred quickly to an air-dried polarimeter tube (2 dcm.), and readings were taken as soon as possible, namely, about 2 minutes from zero time in the case of water and pyridine, but about 5 minutes in the case of solutions rich in cresol, which were much more viscous.

6. *The experimental results* are summarised in Tables I, II, and III, and are represented graphically in Figs. 1 and 2. The individual readings have not been reproduced. A complete mutarotation-curve is therefore represented by a single monomolecular coefficient § in the tables, and by a single point on the curves.

TABLE I.

Mutarotation of Glucose in mixtures of Pyridine and Water at 20°.

% H_2O.	k.*
100	0·015
95	0·140
90	*0·258* †
85	*0·274*
80	*0·282, 0·272, 0·269, 0·258*
70	*0·225, 0·277, 0·288*
65	*0·210*
60	*0·190*
50	*0·221, 0·236*
40	0·166, 0·168
30	0·106, 0·100
20	0·046
10	0·012
0	0·0008

TABLE II.

Mutarotation of Tetramethyl Glucose in mixtures of Pyridine and Water at 20°.

% H_2O.	k.
100	0·0128
97·5	0·099
95	0·177
92·5	*0·219*
90	*0·264, 0·261*
85	*0·272, 0·254*
80	*0·267, 0·273*
75	*0·300*
70	*0·317, 0·238*
60	*0·318, 0·291*
50	*0·251*
40	*0·203, 0·179*
30	0·108
20	0·040, 0·042
10	0·0088
0	0·0003

TABLE III.

Mutarotation of Tetramethyl Glucose in mixtures of Cresol and Pyridine at 20°.

% Cresol.	k.
100 ‡	0·0003
99 ‡	0·027
97·5 ‡	0·060
95 ‡	0·082
92·5 to 55·0	Mutarotation too rapid for measurement.
52·5	0·180
49·9	0·148
40·4	0·067
21·1	0·0168
1·62	0·0013
0	0·0003

* $k = 1/t \,.\, \{\log (a_0 - a_\infty) - \log (a_t - a_\infty)\}$. In calculating this coefficient the time was always expressed in *minutes*.

† Values shown in italics correspond with a half-change period of less than 3 minutes and are not regarded as trustworthy.

‡ *m*-Cresol was used for these four solutions, as *o*-cresol is solid at these concentrations.

§ The evidence for the monomolecular character of the curves will be discussed later in another paper.

Even under the most favourable conditions, the fastest mutarotations for which fairly trustworthy data can be given correspond with a velocity coefficient of less than 0·2, since this velocity coefficient already corresponds with a half-change period of only 2·3 minutes. Values greater than this are therefore shown in italics in the tables and are indicated only by a dotted line in Figs. 1 and 2. In the case of glucose, the mixtures which gave the highest velocities also gave cloudy solutions, which were difficult to read; but the general course of the curve can be inferred fairly accurately from the velocity coefficients for stronger and weaker solutions, for which much more concordant values were obtained. The mixtures rich in cresol suffered from the two-fold disadvantage that they were very viscous and showed only a relatively small change of rotatory power; the velocity–concentration curve for pyridine–cresol mixtures therefore includes a longer dotted section than the two curves for mixtures of pyridine and water.

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CCCC.—*Reactions of Organic Thiosulphates.*

By HENRY BELL FOOTNER and SAMUEL SMILES.

ABUNDANT evidence is available showing the instability of the disulphoxides, which are to be regarded as containing the thiol-sulphonate structure ·S·SO_2· (this vol., p. 224), and the ease with which their sulphur chain may be ruptured. To ascertain whether this type of reaction is exhibited by the thiosulphonate group under other structural conditions, the organic sodium thiosulphates, which, owing to the work of Price and Twiss (J., 1907, 91, 2021), may be confidently assumed to have the thiol-sulphate structure, RS·SO_2·ONa, have been examined. In aqueous solution, these substances are very readily decomposed by sodium mercaptides and by alkali cyanide. The former reagent quickly yields at the ordinary temperature sodium sulphite and an insoluble product composed of a disulphide or a mixture of disulphides, according to the mercaptide used,

$$RS{\cdot}SO_3Na + NaSR' = RS{\cdot}SR' + Na_2SO_3.$$

When R and R′ are the same, this product is homogeneous and consists of a symmetrical disulphide, but when they are

dissimilar it is in most cases a mixture of the two possible symmetrical disulphides; only in a few instances has the unsymmetrical disulphide been isolated. This behaviour is closely parallel to that of the disulphoxides (J., 1924, **125**, 176),

$$RS{\cdot}SO_2R + R'SNa = RS{\cdot}SR' + RSO_2Na,$$

and the formation of the mixture of symmetrical disulphides is adequately explained by the secondary reaction of the mercaptide with disulphide (Lecher, *Ber.*, 1920, **53**, 591) :

$$RS{\cdot}SR' + NaSR \rightleftharpoons RS{\cdot}SR + R'SNa.$$

The organic thiosulphates are also quickly decomposed by aqueous alkali cyanide, more than 90% reacting thus :

$$RS{\cdot}SO_3Na + NaCN = RSCN + Na_2SO_3.$$

The products are almost pure and, the yields being excellent, the method is well adapted to the preparation of thiocyanates when the corresponding thiosulphates are available. According to unpublished experiments, the disulphoxides behave in a similar manner,

$$RS{\cdot}SO_2R + NaCN = RSO_2Na + RSCN,$$

but are much less reactive.

The interaction of mercaptans and di-*p*-toluenesulphonyl sulphide (Tröger, *J. pr. Chem.*, 1899, **60**, 117) has also been examined with similar results,

$$(C_7H_7{\cdot}SO_2)_2S + 2RSNa = C_7H_7{\cdot}SO_2{\cdot}SNa + C_7H_7{\cdot}SO_2Na + (RS)_2,$$

the sulphur chain being ruptured with formation of sulphinate and thiosulphonate together with the disulphide corresponding to the mercaptan used.

According, then, to these experiments and others previously made with disulphoxides, the characteristic reactions of the thiolsulphone group in substances of the type $RS{\cdot}SO_2{\cdot}X$ are mainly due to instability of the dithio-system; this group is readily split by alkali mercaptides and with varying ease by other reagents, the activity depending on the character of the group X.

Experiments have also been made with the polythionates. Sodium dithionate is not attacked by alkali mercaptides, but the tri- and tetra-thionates are rapidly decomposed, the disulphide being formed in both cases. The trithionate is resolved into sulphite and thiosulphate, and the tetrathionate into thiosulphate. The completed reactions,

$$Na_2S_3O_6 + 2RSNa = (RS)_2 + Na_2SO_3 + Na_2S_2O_3$$
$$Na_2S_4O_6 + 2RSNa = (RS)_2 + 2Na_2S_2O_3,$$

may be regarded as analogous to the reduction of these substances by sodium amalgam. Strictly quantitative measurements have not

been made, but more than 90% of the materials undergo the reactions indicated. Whilst the constitution of the polythionates is undetermined nothing further can be said of the nature of these reactions but, bearing in mind the known behaviour of mercaptides with the dithio and thiolsulphone systems, the processes are, in the authors' opinion, adequately explained by the structures proposed by Mendeléev for the polythionates. In this connexion, the close resemblance of the behaviour of the trithionate to that of ditoluenesulphonyl sulphide is significant.

Experimental.

Reaction of Organic Thiosulphates with Sodium Mercaptides.—The benzyl and *p*-nitrobenzyl thiosulphates used were prepared by Price and Twiss's method (*loc. cit.*) and the 9-anthryl thiosulphate by Friedländer's (*Ber.*, 1922, **55**, 3969). The sodium mercaptide (1 mol.) and the thiosulphate (1 mol.) reacted rapidly in aqueous solution at the ordinary temperature. After ½ hour, the solution was neutral and contained sulphite with at the most only traces of sulphate. The yield of the precipitated disulphides generally exceeded 95%. The results from six of the cases examined are in the following table :

Mercaptan.	Thiosulphate.	Products.
Benzyl.	Benzyl.	Benzyl disulphide, 99%.
2-Nitrophenyl.	Benzyl.	Benzyl 2-nitrophenyl disulphide, 99%.
9-Anthryl.	Benzyl.	Dianthryl, dibenzyl, and anthryl benzyl disulphides.
2-Nitrophenyl.	4-Nitrobenzyl.	2-Nitrophenyl and 4-nitrobenzyl disulphides.
2 : 5-Dichlorophenyl.	9-Anthryl.	Dianthryl and tetrachlorodiphenyl disulphides.
2-Nitrophenyl.	9-Anthryl.	2-Nitrophenyl and anthryl disulphides.

The symmetrical disulphides named have been previously described.

Benzyl 2-nitrophenyl disulphide separated from alcohol in yellow needles, m. p. 54° (Found : N, 5·4; S, 23·3. $C_{13}H_{11}O_2NS_2$ requires N, 5·05; S, 23·1%). The melting point of an equimolecular mixture of the two symmetrical disulphides was lowered by admixture with this substance.

Benzyl 9-anthryl disulphide was isolated from warm alcohol in yellow prisms, m. p. 128°. When it was mixed with equimolar proportions of dibenzyl and dianthryl disulphides its melting point was lowered (Found : C, 75·5; H, 4·4; S, 19·5. $C_{21}H_{16}S_2$ requires C, 75·9; H, 4·8; S, 19·3%).

Reaction of Organic Thiosulphates with Alkali Cyanide.—On

mixing aqueous solutions of potassium cyanide and the thiosulphate (equal mols.) reaction quickly ensued. It was completed by keeping the mixture for various periods, generally ½ hour, or was assisted by maintaining the temperature at about 30°. The yield of thiocyanate, which separated practically pure in most cases, was almost quantitative and a corresponding amount of sulphite was found in the aqueous liquor. In this way, the following thiocyanates were isolated.

Benzyl thiocyanate, m. p. 41° (Found: N, 9·7; S, 21·3. Calc., N, 9·4; S, 21·5%).

2-Nitrobenzyl thiocyanate, m. p. 71° (Found: N, 14·7. Calc., N, 14·4%). Cassira (*Ber.*, 1892, **25**, 3028) gives the m. p. of this substance as 75°.

4-*Nitrobenzyl thiocyanate*, colourless prisms, m. p. 79°, from warm alcohol (Found: N, 14·1; S, 16·4. $C_8H_6O_2N_2S$ requires N, 14·4; S, 16·5%).

9-*Anthryl thiocyanate*, pale yellow needles, m. p. 181°, from hot alcohol (Found: N, 6·4; S, 13·4. $C_{15}H_9NS$ requires N, 6·5; S, 13·6%).

Reaction of Di-p-toluenesulphonyl Sulphide with Mercaptans.—An alcoholic solution of the mercaptide (2 mols.) and the sulphide (1 mol.) containing 5 g. in 100—150 c.c. was warmed on the water-bath and the solvent was then evaporated, water being added towards the completion of the process. The insoluble product, in all the cases examined, was the disulphide corresponding to the mercaptan taken. The solution, containing sulphinate and thiosulphonate, was acidified and gently warmed to decompose the latter; after the addition of aqueous sodium carbonate the coagulated sulphur was collected, and the filtrate again rendered acid. The liberated sulphinic acid was in each case *p*-toluenesulphinic acid.

The disulphides obtained in this way from 2 : 5-dichlorophenyl, 6-methoxy-*m*-tolyl, and 3-chloro-6-methoxyphenyl mercaptans were identified by comparison with authentic samples from other sources.

Reaction of Sodium Tetrathionate with Mercaptides.—A typical experiment was as follows. A solution of 5 g. (2 mols.) of 6-methoxy-*m*-tolyl mercaptan in a small volume of alcohol was exactly neutralised with aqueous sodium hydroxide and added to a stirred solution of 7·5 g. (1 mol.) of sodium tetrathionate in 200 c.c. of water. The disulphide separated at once, but the mixture was kept for an hour before the solid was collected. The filtrate contained thiosulphate but no sulphite. Determinations of the iodine value were made and the roughly quantitative data obtained agreed well with the equation previously given; *e.g.* (*a*) 6-methoxy-

m-tolyl mercaptan: I value, 92%; disulphide, 97% of theory, (*b*) 3-chloro-6-methoxyphenyl mercaptan: I value, 95%; disulphide, 95%, (*c*) 2 : 5-dichlorophenyl mercaptan: I value, 98%; disulphide, 99%.

Reaction of Sodium Trithionate with Mercaptans.—The method of experiment was the same as the preceding. With benzyl, 6-methoxy-*m*-tolyl, and 2 : 5-dichlorophenyl mercaptans, the disulphides were isolated in 99—100% of the yields required by the equation previously given, whilst the approximate iodine values of the filtrates were about 90%. Estimation of the sulphite in the case of 6-methoxy-*m*-tolyl mercaptan showed 99—100% of the theoretical amount of this salt to be present in the aqueous liquor.

We desire to thank the Department of Scientific and Industrial Research for a grant which enabled one of us to take part in this work.

KING'S COLLEGE, LONDON. [*Received, November 3rd,* 1925.]

CCCCI.—*Observations on the Claisen Reaction.*

By GILBERT T. MORGAN and EUSEBIUS HOLMES.

UNTIL recently the condensation of the higher methyl monoketones with esters under the influence of sodium had only been investigated up to the homologues containing the radicals *n*-hexyl and *n*-nonyl. The present investigation was undertaken to find out where, and if possible why, the reaction stopped when applied to methyl ketones containing also one of the higher alkyl radicals.

The nomenclature throughout this paper is based on the following condensation with ethyl acetate:

$$C_nH_{2n+1}\cdot CO\cdot CH_3 \longrightarrow C_nH_{2n+1}\cdot CO\cdot CH_2\cdot CO\cdot CH_3.$$

It is shown that, under the conditions stated, the reaction proceeds quite normally from $n = 7$ to $n = 19$, a satisfactory yield of 1 : 3-diketone being obtained in every case.

The general method of procedure has been to convert the corresponding fatty acid into its barium salt and to distil this with three molecular proportions of anhydrous barium acetate in a specially constructed flat vacuum pan (Morgan and Holmes, *J. Soc. Chem. Ind.*, 1925, **44**, 108T). The crude product was purified and subjected to the Claisen condensation with sodium and ethyl acetate, the sodium salt of the enolic form of the β-diketone being treated with acetic acid and the liberated diketone precipitated

and purified as its co-ordinated copper derivative. The acids $C_nH_{2n+1}\cdot CO_2H$, where $n = 10, 12, 14, 18$, were obtained by oxidising the methyl ketone from the next higher naturally occurring acid, to give acetic acid and the required acid, from which mixture the latter was isolated as its relatively insoluble barium salt.

The copper salts of the β-diketones are blue, as are the lower members of the series, but the colour becomes less pronounced as the homologous series is ascended. The diketones from $n = 7$ to 19 have been obtained as solids at the ordinary temperature, whilst the monoketones from $n = 10$ upwards are colourless solids with progressively higher melting points.

Since this work originally arose out of the researches on cyclic tellurium compounds of bactericidal potency, it is of interest to note that Mr. C. J. A. Taylor (this vol., p. 2615) has found it possible to prepare *cyclo*telluropentanedione dichlorides reducible to bactericidal *cyclo*telluropentanediones in the case of the following diketones, all of which are described in the present paper : *n*-octoylacetone, *n*-nonoylacetone and *n*-duodecoylacetone (lauroylacetone). These are the only ones so far condensed with tellurium tetrachloride, but it appears probable that the whole of the series would give similar results.

Experimental.

In the case of the lower members of the series, $n = 9$ and below, the procedure was as described below in the case of *n*-octoylacetone. For the higher members, three to nine mols. of the ester were employed, no preliminary cooling being necessary. After heating under reflux for from 4 to 5 hours, the mixture was poured on to ice as before.

The mixtures were then neutralised with acetic acid, and saturated cupric acetate was run in. In most cases, the copper salts of the diketones were precipitated at once, but for the higher ones, $n = 15$ and upwards, it was found necessary to add alcohol to bring the reagents together.

The free diketones were obtained by treating the copper salts with dilute sulphuric acid in the presence of ether, which was subsequently removed. The lower diketones were purified by vacuum distillation, the higher ones by crystallisation from alcohol.

n-*Octoylacetone*.—*n*-Heptyl methyl ketone (35 g.), obtained by the dry distillation of barium *n*-octoate with barium acetate (3 mols.), was added to ethyl acetate (2·5 mols.), the mixture cooled to 0°, and sodium (1 atom.) added in the form of thin slices. After 12 hours, the mixture was heated under reflux for 3 hours, allowed to cool, and poured on to ice. The liquid was then made very

slightly acid with dilute acetic acid, and the oily layer of liberated diketone precipitated with a saturated solution of cupric acetate. After being stirred at intervals for ½ hour, the precipitate was collected and washed with a little water and cold alcohol. A yield of 26 g. represented 47·8%. Two subsequent batches gave yields of 41·0 and 48·6%, respectively.

Crystallised successively from alcohol and benzene, the *copper* salt was obtained in pale blue needles and melted at 118°.

The salt (0·5 g.) was shaken with a few c.c. of dilute sulphuric acid in the presence of a little ether. The acid layer was separated, and a water washing of the ether layer added. The copper was precipitated by means of caustic potash, and weighed as the oxide (Found: Cu, 14·6; C, 61·6; H, 8·85. $C_{22}H_{38}O_4Cu$ requires Cu, 14·8; C, 61·45; H, 8·8%).

The *n*-octoylacetone recovered from the copper salt had the characteristic odour of the β-diketones of this series, and boiled at 248°/755 mm. and 118°/5 mm.

n-*Nonoylacetone*.—A quantity of the corresponding ketone from a reputed pure specimen of barium pelargonate (23 g.) was added to 37 g. of pure dry ethyl acetate, and 3·8 g. of sodium were added to the cooled mixture. The *copper* salt of a diketone was obtained by the general method and weighed 26·3 g., a yield of 68·8%. Recrystallised from benzene, it melted at 107°, and was of the expected pale blue colour (Found: Cu, 13·9. $C_{24}H_{42}O_4Cu$ requires Cu, 13·9%).

Since the above melting point was not in accord with those of the other members of the series, and, furthermore, other discrepancies arose when the diketone was condensed with tellurium tetrachloride, another specimen of pelargonic acid was obtained and the reactions were repeated. Again the copper salt of a diketone was obtained, purified, and analysed (Found: Cu, 13·75; C, 63·05; H, 9·4. Theory requires Cu, 13·9; C, 62·9; H, 9·2%).

This specimen melted at 115·5°, a value bringing it in line with its homologues. It appears probable that the earlier specimen of acid contained an acid isomeric with pelargonic acid but having a branched chain remote from the carboxyl group.

The *n*-nonoylacetone recovered from the copper salt boiled at 150°/15 mm.

n-*Decoylacetone*.—This diketone has been described (Morgan and Holmes, J., 1924, **125**, 760; *J. Pharm. Soc.*, June 14, 1924).

n-*Undecoylacetone*.—*n*-Decyl methyl ketone, obtained from the corresponding undecoic acid, which was itself prepared by the ketone and acidified dichromate degradation of lauric acid, was condensed with sodium and ethyl acetate (6 mols.). The

yield of *copper* salt was 3·9 g. (70%). After crystallisation from benzene the salt melted at 112° (Found: Cu, 12·4; C, 65·6; H, 10·0. $C_{28}H_{50}O_4Cu$ requires Cu, 12·4; C, 65·4; H, 9·7%).

The free diketone was obtained as a colourless solid melting at 28°.

n-*Duodecoylacetone* (*Lauroylacetone*).—Three separate batches of the monoketone obtained from lauric acid were condensed with 3, 6, and 9 molecular proportions of ethyl acetate, respectively, the period of refluxing being extended to 4 hours. The yields of *copper diketone* from 5 g. of ketone were 2·6 g., 3·45 g. (50·2%), and 3·40 g., respectively. It appears that the optimum yield of rather more than 50% was reached by using 6—8 molecular proportions of ester in the condensation. The pure salt melted at 112·5° (Found: Cu, 11·7; C, 66·6; H, 10·3. $C_{30}H_{54}O_4Cu$ requires Cu, 11·7; C, 66·5; H, 10·0%).

The free diketone was a colourless solid of melting point 31—32°.

n-*Tridecoylacetone*.—Myristic acid was converted into the barium salt and dry-distilled with barium acetate. The resulting methyl ketone was then oxidised with acid sodium dichromate to give the next lower acid, which, on subsequent distillation of its barium salt, gave the duodecyl methyl ketone. This (5 g.) was condensed with ester to give 3·7 g. of the *copper diketone*, a yield of 54%. The pure salt melted at 111° (Found: Cu, 11·2. $C_{32}H_{58}O_4Cu$ requires Cu, 11·2%).

The pure *diketone* obtained from the copper derivative was a colourless solid melting at 35°. It had scarcely any odour and gave the red ferric coloration with alcoholic ferric chloride only on warming (Found: C, 75·4; H, 11·7. $C_{16}H_{30}O_2$ requires C, 75·6; H, 11·8%).

n-*Tetradecoylacetone* (*Myristoylacetone*).—Five g. of the ketone obtained from myristic acid were subjected to the Claisen reaction, giving 3·42 g. of *copper* salt (yield 52%) which, after crystallisation from alcohol and from benzene, melted at 112° (Found: Cu, 10·5. $C_{34}H_{62}O_4Cu$ requires Cu, 10·6%).

The free *diketone* melted at 39° (Found: C, 76·1; H, 12·3. $C_{17}H_{32}O_2$ requires C, 76·1; H, 11·9%).

n-*Pentadecoylacetone*.—*n*-Tetradecyl methyl ketone was prepared from palmitic acid by the general degradation process. Condensed with ethyl acetate, it gave 2·25 g. of the *copper diketone*, a yield of 35%. The purified salt melted at 111° (Found: Cu, 10·5. $C_{36}H_{66}O_4Cu$ requires Cu, 10·2%).

The colourless *diketone* melted at 42° (Found: C, 76·4; H, 12·0. $C_{18}H_{34}O_2$ requires C, 76·6; H, 12·1%).

n-*Hexadecoylacetone* (*Palmitoylacetone*).—*n*-Pentadecyl methyl

ketone (5 g.) obtained from palmitic acid was condensed with ethyl acetate (7 mols.) by the general method, the time of refluxing being raised to 5 hours. The copper salt (yield 2·2 g.; 34%) after purification melted at 112° (Found: Cu, 9·6. $C_{38}H_{70}O_4Cu$ requires Cu, 9·7%).

The decomposition of the copper salt by dilute sulphuric acid in presence of ether took an excessive time. Accordingly, in this case and in the case of all the higher members of the series, the copper derivative was suspended in water, an equal volume of concentrated acid added, and the mixture allowed to cool before being extracted with ether.

The free *diketone* crystallised from alcohol in colourless plates, m. p. 49° (Found: C, 76·8; H, 12·3. $C_{19}H_{36}O_2$ requires C, 77·0; H, 12·2%).

n-*Heptadecoylacetone* (*Margaroylacetone*).—The condensation of the ketone (5 g.) obtained from margaric acid was carried out with 3, 6, and 9 mols. of ester, respectively, the time of refluxing being 5 hours. The yields of *copper* salt were 0·35 g., 1·7 g. (27%), and 1·4 g., and of recovered ketone, 4·0 g., 2·5 g., and 2·9 g., respectively. In each case, a small amount of copper margarate was produced. The copper salt of the diketone was washed with cold ether. The unchanged ketone was then separated from the copper margarate in the washings by acidification, treatment with barium acetate, and filtration of the insoluble barium salt.

The pure copper salt melted at 112° (Found: Cu, 9·3. $C_{40}H_{74}O_4Cu$ requires Cu, 9·3%), and the free *diketone* at 51° (Found: C, 77·3; H, 12·3. $C_{20}H_{38}O_2$ requires C, 77·4; H, 12·3%).

n-*Octadecoylacetone* (*Stearoylacetone*).—In a repetition of previous work, 10 g. of *n*-heptadecyl methyl ketone were condensed with ethyl acetate (35 mols.) and sodium, and 0·75 g. of *copper diketone* was obtained on adding cupric acetate and alcohol to the reaction mixture (yield 6%). With 8 mols. of ester, 6·9 g. of copper salt were obtained (yield 55%). No diketone copper salt was ever obtained until alcohol was added to the reaction mixture, this accounting for some of the earlier negative results. The purified salt melted at 113° (Found: Cu, 9·0. $C_{42}H_{78}O_4Cu$ requires Cu, 9·0%).

The free *diketone* crystallised from alcohol in colourless plates, m. p. 52·5°, and gave a red coloration with alcoholic ferric chloride on warming (Found: C, 77·5; H, 12·4. $C_{21}H_{40}O_2$ requires C, 77·8; H, 12·35%).

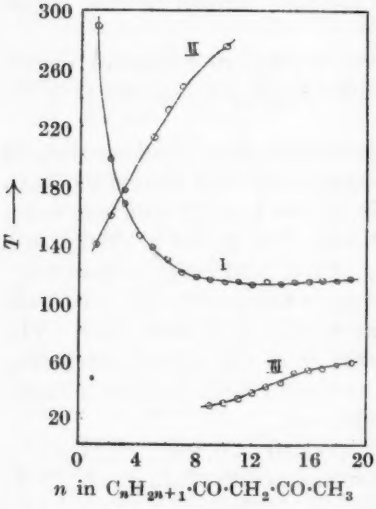
n-*Nonadecoylacetone*.—*n*-Octadecyl methyl ketone was obtained from the C_{20} acid by the general degradation process. Condensing with ethyl acetate gave a 32% yield of a *copper diketone*, some

unchanged ketone being recovered. The pure salt, crystallised from benzene, melted at 112·5° (Found : Cu, 8·6. $C_{44}H_{82}O_4Cu$ requires Cu, 8·6%).

The recovered *diketone* consisted of thin plates, m. p. 55° (Found : C, 77·9; H, 12·5. $C_{22}H_{42}O_2$ requires C, 78·1; H, 12·4%).

n-*Eicosanoylacetone*.—Potassium erucate was fused with caustic potash, giving acetic acid and the normal C_{20} acid, eicosanic acid. After purification, this was converted into its barium salt, which was then distilled with barium acetate. The *n*-nonadecyl methyl ketone obtained was condensed with ethyl acetate in the general manner to give the corresponding *copper* derivative, 5 g. yielding 1·75 g. (28·4%). Crystallised from benzene, the salt melted at 114° (Found : Cu, 8·15. $C_{46}H_{86}O_4Cu$ requires Cu, 8·3%).

Fig. 1.



The free *diketone* melted at 57° (Found : C, 78·4; H, 12·6. $C_{23}H_{44}O_2$ requires C, 78·4; H, 12·5%).

In the diagram, curve I shows a noteworthy change in the fusibility of copper β-diketones with lengthening of the carbon chain. Curves II and III indicate the boiling points of the lower diketones and the melting points of the higher diketones, respectively.

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University of Birmingham,
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CCCCII.—*The Relation of Homogeneous to Catalysed Reactions. The Catalytic Decomposition of Hydrogen Iodide on the Surface of Platinum.*

By Cyril Norman Hinshelwood and Robert Emmett Burk.

The results of several previous investigations (this vol., pp. 327, 1105, 1552; *Proc. Roy. Soc.*, 1925, *A*, **108**, 211) have rendered

probable the conclusion that simple gaseous decompositions, which as homogeneous reactions are bimolecular, become unimolecular when they take place in contact with the surface of a solid catalyst. Thus, for example, the thermal decomposition of nitrous oxide, $2N_2O = 2N_2 + O_2$, as an uncatalysed reaction depends upon the collision of two molecules, but the reaction which takes place upon the surface of gold appears to be simply $N_2O = N_2 + O$, followed by the combination of atomic oxygen to the molecular form. The decompositions of nitrous oxide on the surface of platinum, and of ammonia on the surface of platinum have also been shown to be unimolecular.

It is not always possible to decide from measurements of reaction rate whether a catalytic reaction is unimolecular or bimolecular. If the active surface of the catalyst is completely covered with adsorbed molecules—' saturated '—then the reaction rate is independent of the pressure of the gas. The reaction appears to be of ' zero order.' When, on the other hand, the adsorption is small, the chance of a group of n molecules occupying positions on the surface near enough for interaction to be possible is proportional to the nth power of the total number adsorbed, and this in turn to the nth power of the pressure of the gas. The ' order ' of the reaction obtained from kinetic measurements gives under these conditions the number of molecules actually participating in the decomposition. An intermediate condition is possible, when the adsorption is neither very large nor quite small, where a bimolecular reaction might simulate a unimolecular reaction over a small range of pressure. But if the reaction order appeared to be unity by a coincidence of this kind, it would vary very markedly both with pressure and with temperature, as may easily be seen. This state of affairs would readily be detected, and the results discounted, so that in general we may say that unless the reaction order is zero it gives the number of molecules participating in the change.

The decomposition of ammonia on tungsten, and of hydrogen iodide on gold are both approximately of order zero; consequently we cannot conclude how many molecules are involved. The homogeneous decomposition of hydrogen iodide is one of the best known bimolecular reactions. We were anxious therefore to find a catalyst at the surface of which the true order of the heterogeneous reaction could be found. Platinum fulfils these conditions. The reaction takes place in the simple unimolecular manner, $HI = H + I$, followed by the combination of atomic hydrogen and iodine to form molecules.

This illustrates once more the fundamental importance in hetero-

geneous catalysis of the affinity which metal surfaces possess for free atoms.

Method of Experiment.—The hydrogen iodide was prepared by the action of phosphoric acid on potassium iodide and purified by fractional distillation from liquid air, the middle fraction being collected in evacuated blackened glass holders.

The decomposition was allowed to take place at the surface of a heated platinum wire and measured exactly as described for the corresponding experiments with a gold wire (this vol., p. 1552). The reaction vessel was kept in ice. Since the iodine condensed, the reaction $2HI = H_2 + I_2$ is attended by a decrease in pressure which allows the rate to be measured by simple manometric means.

That the action of the platinum wire was 'catalytic,' and that the wire was not attacked by the iodine was shown by the fact that the theoretical change in pressure was observed after complete decomposition, and by the fact that the resistance of the wire remained absolutely unchanged during the whole series of experiments. Its catalytic activity, moreover, remained steady. The mercury in the manometer was protected from the action of the hydrogen iodide by a buffer of hydrogen in the capillary tube leading to the decomposition bulb.

Influence of the Pressure of the Hydrogen Iodide.—Three typical experiments showing the course of the reaction at different temperatures will first be recorded: t is the time in seconds, x the percentage change, and k the unimolecular velocity coefficient.

670°. 200 Mm. HI. 100 Mm. H_2.			563°. 200 Mm. HI. 100 Mm. H_2.			439°. 200 Mm. HI. 100 Mm. H_2.		
t.	x.	$k \times 10^4$.	t.	x.	$k \times 10^4$.	t.	x.	$k \times 10^4$
100	22	24·9	120	12	10·6	600	13	2·32
200	41	26·4	300	27	10·3	1200	26	2·50
300	56	27·4	600	47	10·6	1800	38	2·65
400	64	25·6	900	61	10·5	2400	45	2·49
500	72	25·5	1200	71	10·4	3300	55	2·42
600	76	24·0	1500	78	10·1	4200	63·5	2·40
						6000	74·5	2·28

The influence of the pressure of the hydrogen iodide is shown by the following values found at 563°. 100 Mm. of hydrogen were present in each experiment.

Press. of HI (mm.)	100	200	300
k	0·00118	0·00105	0·00095

The values of k are sufficiently independent of pressure to show that the reaction is unimolecular. The slight dropping off was traced to the circumstance that hydrogen has a small but definite retarding effect on the reaction. When the initial pressure of

hydrogen iodide is great, the pressure of hydrogen at every stage of the reaction is greater than when the initial pressure of hydrogen iodide is small. The slight falling off in rate due to the adsorption of hydrogen by the wire is shown by the following table. 200 Mm. of hydrogen iodide were used in each experiment.

Press. of H_2 (mm.)	0	100	200
k (average)	0·00126	0·00105	0·00092

The Influence of Temperature.—This is shown in the following table. The values of k are those corresponding to a hydrogen pressure of 100 mm.

T (abs.)	943°	836°	712°
k	0·00268	0·00105	0·000244
E (cals.)	13,700	13,850	

Mechanism of the Reaction.—We suggest the simplest possible interpretation of the results, namely, that the reaction at the surface of the platinum is the simple change $HI = H + I$. The apparently unimolecular course could be explained in another way by assuming that there existed one complete layer of hydrogen iodide molecules on the surface of the catalyst and that reaction took place when a molecule from the gas phase struck one of the molecules in this layer. There are, however, several vital objections to this. First, there is abundant evidence to show that where two molecules interact in heterogeneous reactions they must in general both be actually adsorbed. This is shown by the fact that in reactions where A and B interact excess of either A or B can actually retard the reaction by displacing the other from the surface. Secondly, if there is a complete layer there is no reason why the molecules in it should not react among themselves instead of waiting for impacts from the gas phase. Thirdly, if the heterogeneous reaction depended upon impacts from the gas phase, the rate could never become independent of pressure as it does when it takes place at the surface of gold.

Attention may be directed to one further point of interest which emerges from these experiments. The retarding effect of hydrogen on the reaction is but slight. When the catalytic decomposition of ammonia was investigated on the same wire—and actually at a higher temperature—it was found to be retarded in a most pronounced manner by hydrogen. It cannot be argued that hydrogen iodide is too strongly adsorbed to be displaced by hydrogen whilst ammonia is easily displaceable, because the course of a unimolecular reaction can be revealed only when the adsorption is small. Hence we must conclude once more that different reactions are provoked at different points ('active centres') on the catalytic surface.

Summary.

In continuation of a general investigation of the influence of catalytic surfaces on reactions which in the homogeneous gas phase are bimolecular, it has been shown that the thermal decomposition of hydrogen iodide in contact with platinum is kinetically unimolecular. Reasons are given for believing that this proves the decomposition to take place in the simple manner $HI = H + I$.

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CCCCIII.—*Oxidation of Ethyl Ether to Oxalic Acid in Presence of Uranyl Nitrate.*

By SYDNEY WILLIAM ROWELL and ALEXANDER SMITH RUSSELL.

WHEN uranyl nitrate dissolved in ether is exposed to sunlight in presence of water a yellow precipitate sometimes forms in the aqueous layer, especially after the solution has been standing in the light for some days; at other times, a black, slimy mass forms in the aqueous layer. These compounds are the subject of the present investigation. There is only one reference in the literature to the composition of the yellow compound (Soddy, "Chemistry of the Radioelements," 1911, p. 32). Soddy found that a yellow powder of empirical formula UCH_4O_6 remained after distilling the ether from an ethereal solution of uranyl nitrate. On decomposition, this compound formed a basic carbonate which lost carbon dioxide and water at 200—300°.

EXPERIMENTAL.

Preparation of the Yellow Compound.—In a typical experiment, a mixture of 60 g. of ethyl ether, 60 g. of uranyl nitrate and 20—60 g. of water, after being shaken until the nitrate dissolved, was exposed to bright sunlight for periods up to 24 hours. The ether was then removed by distillation at as low a temperature as possible, and the aqueous solution evaporated. On cooling, there separated a yellow compound mixed with uranyl nitrate which was freed from the latter by washing with cold water, in which the former was comparatively insoluble. The yield was poor and rarely exceeded 12 g. The yellow compound was found to be identical in properties with the normal hydrated oxalate of uranium, $UO_2C_2O_4,2H_2O$ (Found: U, 60·5; C_2O_4, 22·2; H_2O, 9·7; C, 6·1; H, 1·2. Calc., U, 60·4; C_2O_4, 22·3; H_2O, 9·1; C, 6·1; H, 1·0%).

Uranium was determined gravimetrically as U_3O_8, and oxalate volumetrically.

Formation of a New Basic Oxalate of Uranium.—In a few of the above experiments the compound which resulted appeared different from the normal oxalate; it had a lighter yellow colour. It gave the usual reactions of an oxalate (Found: U, 68·0; C_2O_4, 12·0%). The basic oxalates which correspond with the normal oxalates would be $U(OH)_4,UO_2C_2O_4,2H_2O$ and $UO_2(OH)_2,UO_2C_2O_4,2H_2O$, depending whether the uranium in the hydroxide is quadri- or sexa-valent. The former of these contains U, 68·0; C_2O_4, 12·6% and the latter U, 68·2; C_2O_4, 12·6%. Either of these might be the compound analysed above. Since the compound $U(OH)_4$ is stabler than $UO_2(OH)_2$, we are inclined to prefer the first formula. It may be written UCH_4O_6, which is identical with that of Soddy's product. The formula of the other product, so written, differs, however, only by a single hydrogen atom. There is no doubt that a basic oxalate is formed by the interaction of uranyl nitrate and ether in the presence of sunlight and it is probable that Soddy's product was this oxalate.

Formation of Uranous Hydroxide.—We find that when uranyl nitrate in solution in ether is neutralised so that a precipitate is just not formed and exposed to sunlight for periods of a few hours, there settles from solution a black or greenish-black, slimy precipitate which accompanies the basic and normal oxalates. It is not formed in solutions of uranyl nitrate containing free nitric acid. It resembles the product obtained by adding ammonia to a solution of a uranous salt, namely $U(OH)_4$, and this composition was confirmed by analysis (Found: U, 78·0. Calc., U, 77·8%). These observations are in agreement with the work of Aloy and Rodier (*Bull. Soc. chim.*, 1920, **27**, 101; 1922, **31**, 246), and of Aloy and Valdiguié (*ibid.*, 1925, **37**, 1135), who found that in neutral solution uranium salts on exposure to sunlight in the presence of certain organic compounds yield a black or a violet precipitate, the former being uranous hydroxide and the latter of composition $U_3O_8,2H_2O$, through partial reduction of the uranyl salt. It is evident from these results that the composition of these lower oxides, like that of the oxalates, varies with the conditions in which they are formed.

Suggested Mechanism of the Reaction.—In the absence of sunlight, none of the products described above is formed. Exposure to sunlight is therefore essential to the reactions. The oxalates formed are not oxidation products of an impurity in the ether, for the most carefully purified ether gave the oxalate, and addition of alcohol, the most likely impurity, did not increase the yield. Moreover, no oxalate resulted when alcohol replaced ether in the solution

of uranyl nitrate, although we found, as Aloy and his co-workers did, that it favours the formation of a hydroxide of uranium in neutral solution. No oxalate was obtained when other uranyl salts replaced the nitrate. Ebelman (*Ann. Chim. Phys.*, 1842, **5**, 198) first pointed out that solutions of the uranyl salts of strong acids were changed by sunlight in presence of an oxidisable compound, acquiring a green colour which we now know to be due to uranous salts, and this work has been greatly extended by Aloy and co-workers (*loc. cit.*). On their view, if A be an acceptor of oxygen, *e.g.*, alcohol, and uranyl nitrate the salt considered, the reaction proceeds in sunlight as $UO_2(NO_3)_2 + 2HNO_3 + A = U(NO_3)_4 + H_2O + AO$ in presence of a sufficiency of nitric acid. If sufficient acid be not present, it is to be expected that some uranous hydroxide would be formed, and this is what we have found. When ether is the acceptor, it is oxidised finally, we find, to oxalic acid. In presence of uranyl ion and free nitric acid, this would be expected to form the normal oxalate as it does; in presence of insufficient acid, a mixture of the normal oxalate and uranous hydroxide or a compound of these would be expected to form. We find the latter.

The manner of oxidation of ether to oxalic acid has not been previously considered in the literature. We suggest the following. Ether is oxidised to diglycol when the uranyl is reduced to the uranous ion by sunlight. Part of the diglycol is oxidised by nitric acid to diglycollic acid and part hydrolysed to glycol, which is then further oxidised by nitric acid to oxalic acid, thus :

$$\text{Ether} \longrightarrow \text{diglycol} \begin{cases} \nearrow \text{diglycollic acid.} \\ \searrow \text{glycol} \longrightarrow \text{oxalic acid.} \end{cases}$$

It is, of course, known that diglycol is oxidised by nitric acid partly to oxalic acid but mostly to diglycollic acid. It has not yet been possible to test this scheme by showing the presence of either diglycol or diglycollic acid.

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CCCCIV.—*Polymerisation of β-Glucosan. The Constitution of Synthetic Dextrins.*

By JAMES COLQUHOUN IRVINE and JOHN WALTER HYDE OLDHAM.

ONE method of approach to the constitutional problems of the polysaccharides is through the study of anhydro-hexoses, and the discovery by Pictet and his collaborators that β-glucosan can be prepared conveniently by the dry distillation of starch acquires a special importance in this connexion. 1 : 6-Anhydroglucose has in this way been rendered available in quantity and its properties have been examined in detail by Pictet and others. One of the most striking of the new observations is that the compound is readily polymerised, the reaction $n(C_6H_{10}O_5) \longrightarrow (C_6H_{10}O_5)_n$ proceeding readily when β-glucosan is heated, either alone or in the presence of catalysts. Thus, when fused with platinum black, glucosan is converted into an amorphous powder, to which the formula $(C_6H_{10}O_5)_4$ applies, and this displays the general properties of a dextrin, yielding glucose on hydrolysis (Pictet, *Helv. Chim. Acta*, 1918, **1**, 226). Pictet, finding platinum black uncertain in its action, improved the method by using zinc chloride as a catalyst (*ibid.*, 1921, **4**, 788) and he also varied the procedure by conducting the polymerisation under both reduced and increased pressure. Four definite compounds were obtained under these conditions :

Polymeride.	$[\alpha]_D$.	Pressure.
1. Diglucosan	+ 28·2°	15 mm.
2. Tetraglucosan	+111·9°	1 atmos.
3. Hexaglucosan	+ 94·1°	4·6 ,,
4. Octaglucosan	+ 72·8°	13·2 ,,

Although there seems no theoretical limit to the number or variety of possible polymerides, the above list includes only compounds in which glucosan molecules may be regarded as having become associated in multiples of two. The mode of attachment of the parent molecules has hitherto, save in one case, remained obscure, but Pictet has recorded the abnormality that the polymerides yield only diacetates or dibenzoates in place of the tri-derivatives to be expected.

By arrangement with Professor Pictet, we have been engaged on the constitutional study of the polyglucosans and take this opportunity of expressing our thanks for his courteous permission to extend his work. The completion of the investigation, which was commenced four years ago, has been delayed in consequence of the complexity of the results, and, in the meantime, Pringsheim

has described the application of the methylation process to tetraglucosan (*Ber.*, 1922, **55**, 3001). No difficulty was apparently experienced by him in obtaining complete alkylation and, on hydrolysis of the product, both tetramethyl and dimethyl glucose were obtained. This is a striking result, but, as shown by Pringsheim, it is in itself insufficient to discriminate between two alternative structures for tetraglucosan.

In order to obtain an adequate view of the mechanism of the polymerisation of glucosan, it is necessary to study the constitution of a variety of polymerides displaying a progressive increase in molecular complexity, and this we have accomplished. In repeating Pictet's experiments little success was attained in using platinum black as a catalyst and, after numerous attempts to find a superior reagent, we adopted the method of heating glucosan at 250° in the presence of zinc dust. The polymerisation was conducted in a vacuum, the residual air having been washed out with hydrogen and, under these conditions, the change took place without charring or alteration in weight.* As the zinc dust employed contained a trace of chloride, it is possible that the latter is the functional catalyst, as we find that zinc chloride exercises a powerful polymerising effect on glucosan and its derivatives, the reaction in some instances being violent. For many reasons we prefer the use of metallic zinc, and, although polymerides differing from those described by Pictet are produced, we have continued to employ the process, as it proved satisfactory for large-scale working and gave uniform results. It may be remarked, however, that the relative yield of the different dextrins is affected, not only by the catalyst, but also by the temperature, by the duration of heating, and by the scale of working.

In order to obtain polymerides of high molecular weight, it is unnecessary in our experience to work under positive pressures, and all our preparations were carried out at 15 mm. By means of fractional precipitation from aqueous solution the polymerides were separated into three main fractions, which, in order of increasing solubility, showed the following progressive diminution in

* It may be mentioned that glucosan is much less stable at high temperatures, particularly in the presence of acids, than the method of preparing the compound would suggest. Nevertheless Venn (*J. Text. Ind.*, 1924, **15**T, 414), having found that the yield of glucosan from cellulose is greatest when the acidity of the distillate is lowest, states that this result is opposed to our views as to the origin of the hexosan. It would have been surprising if any other result had been obtained and Venn's observation, which amounts to no more than the statement that the best yields of glucosan are obtained under the most favourable experimental conditions, has no bearing on the mechanism of the reactions in which glucosan is formed.

specific rotation. Dextrin I + 83·9°; Dextrin II + 60·7°; Dextrin III + 29·9°. In marked distinction to the products described by Pictet, all the dextrins yielded a definite triacetate, and the presence of three hydroxyl groups per C_6 unit was confirmed by methylation. The convenient solubilities of these trimethyl dextrins rendered possible the determination of their molecular weights in benzene solution and, in this way, the parent compounds were characterised as containing respectively seven, four, and three glucosan units.

Methylated product.	Mol. wt. (found).	Mol. wt. (calc.).	Parent compound.
Trimethyl Dextrin I	1446	1428	Heptaglucosan
,, ,, II	874	816	Tetraglucosan
,, ,, III	595	612	Triglucosan

This does not exhaust the list of polyglucosans, as we have also obtained other isomerides, and it is evident that both odd and even numbers of glucosan molecules are capable of forming polymerides. Further, it is clear that the tetraglucosan examined in the course of the present investigation is different from that described by Pictet and subsequently examined by Pringsheim. The distinction is shown in the specific rotations of the compounds, in the m. p. of the triacetates prepared from them and, most emphatically, in the different behaviour of their methylated derivatives on hydrolysis.

The methylated dextrins, which may now be termed hepta-, tetra-, and tri- (trimethyl glucosan), respectively, were examined so as to give an insight into the mode of attachment of the constituent hexose chains, the information being derived by identifying the methylated glucoses formed on hydrolysing each compound. In order to indicate the significance of these results, it may be recalled that, although it is customary to distribute the hydroxyl groups equally among the C_6 units of a polysaccharide or allied compound, this allocation is based on an assumption and should be subjected to experimental test in each case. Thus, cellulose and hexa-amylose (Irvine, Pringsheim, and Macdonald, J., 1924, **125**, 942), which are isomeric with the dextrins now under consideration, give trimethyl derivatives and these, in turn, yield on hydrolysis 2 : 3 : 6-trimethyl glucose and no other sugar. It follows that the hydroxyl groups in the parent compounds are uniformly distributed, *i.e.*, each C_6 unit carries three hydroxyls arranged in the same positions. Were this not the case, isomeric trimethyl glucoses would be formed or, alternatively, a mixture of methylated sugars, such as tetramethyl and dimethyl glucoses, giving the same average composition.

In marked contrast to natural polysaccharides, the synthetic

dextrins afford striking examples of compounds constituted on an entirely different model in that the hydroxyl groups are not attached uniformly to the individual C_6 units. We have already shown (J., 1921, **119**, 1744) that when β-glucosan is subjected to consecutive methylation and hydrolysis it gives 2 : 3 : 5-trimethyl glucose and, on the basis of analogy, it might reasonably be expected that the same end-product would be obtained from a polymerised glucosan. Such is not the case. Each trimethyl dextrin was converted into the corresponding methylated methylglucosides and thereafter into the constituent sugars, but the product, in place of being homogeneous, consisted in each case of di-, tri-, and tetramethyl glucose, mixed in proportions which gave the analytical figures required for a trimethyl glucose alone. The individual sugars were separated and two of them were characterised as 2 : 3 : 5 : 6-tetramethyl glucose and 2 : 3 : 5-trimethyl glucose, but the constitution of the dimethyl sugar is still uncertain and two alternatives are possible. Although in this section of our work we did not conduct the separation of the above sugars on quantitative lines, good reasons exist for the belief that hepta-, tetra-, and tri-(trimethyl glucosan) all give the same methylated glucoses, as the physical constants of each mixture were identical.

It is necessary to emphasise that the tetramethyl glucose isolated in these experiments is a genuine scission product of the methylated dextrins, and does not originate in any molecular cleavage during the methylation process. This possibility was carefully excluded, and the result in itself disposes of the idea that the polymerisation of glucosan is merely the union of intact molecules in pairs. The process is evidently complex and consists essentially in the formation of glucosidoglucosides which show a general structural resemblance with the constitutional type ascribed by Hess to cellulose. The development of structural formulæ for the polyglucosans demands, however, a knowledge of the relative proportions of the different methylated glucoses into which they can be transformed. A considerable advance was made by conducting all the operations, from the polymerisation of the glucosan to the separation of the methylated glucoses finally obtained, on strictly quantitative lines. For this purpose large quantities of material were required and a substantial simplification was effected by methylating the total polymerised product and separating the isomerides by vacuum distillation, without isolation of the parent compounds. The first fraction consisted of monomeric trimethyl glucosan, whilst the second was a viscous syrup which was shown to be di (trimethyl glucosan). The remaining syrup, which constituted the largest fraction, was practically non-volatile at 200°/0·4

mm. and, on cooling, it solidified to a clear red glass. As this product contained all polymerides higher than the dimeride, it is termed poly (trimethyl glucosan).

Di(trimethyl glucosan) was converted into the methylglucosides of the constituent sugars, the products being formed in the proportions shown below :

		Yield %. Found.	Calc. for equal mols.
Di(trimethyl glucosan) →	Dimethyl methylglucoside.	46·6	47·1
	Tetramethyl methylglucoside.	53·4	52·9

These proportions were confirmed from the yields of the corresponding sugars when, as before, 2 : 3 : 5 : 6-tetramethyl glucose was isolated together with a dimethyl glucose.

An equally significant result was obtained by similar treatment of poly(trimethyl glucosan), three glucosidic products being obtained in place of two.

		Yield %. Found.	Calc. for equal mols.
Poly(trimethyl glucosan) →	2 : 3 : 5 : 6-Tetramethyl methylglucoside.	35·5	35·3
	2 : 3 : 5-Trimethyl methylglucoside.	33·5	33·3
	Dimethyl methylglucoside.	26·0	31·4
	Monomethyl methylglucoside.	5·0	

As shown by the analytical figures quoted in the experimental part, the small amount of monomethyl methylglucoside is attributable to incomplete methylation and may be added to the yield of the higher homologue.

Discussion is simplified by tabulating the significant facts showing the mutual relationships between glucosan and the polymerides now described.

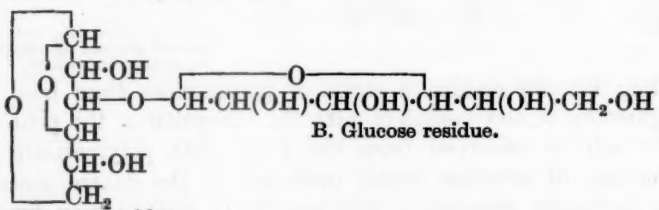
	$[\alpha]_D$ of parent compound. (water)	$[\alpha]_D$ of trimethyl derivative. (MeOH)	Mol. wt. of derivative.	% Methoxyl content of derived glucosides.	Methylated sugars produced.
β-Glucosan ...	−65·4°	−53·2°	212 (204)	50·9	2 : 3 : 5-Trimethyl glucose.
Diglucosan ...	—	+48·3	418 (408)	51·2	2 : 3 : 5 : 6-Tetramethyl glucose. + Dimethyl glucose.
Triglucosan ...	+29·9	+52·8	595 (612)	49·7	2 : 3 : 5 : 6-Tetramethyl glucose. + 2 : 3 : 5-Trimethyl glucose. + Dimethyl glucose.
Tetraglucosan	+60·7	+68·7	873 (816)	49·6	,, ,,
Heptaglucosan	+85·8	+89·4	1446 (1428)	50·4	,, ,,
Polyglucosan	—	—	—	50·6	The above tetra-, tri-, and di-methyl glucoses in exactly molecular proportions.

Including Pictet's results, a series of polymerides from mono- to octa-glucosan is now complete with the exception of the penta-form. It will be observed from the table that polymerisation alters the sign of rotation, which increases, in the dextro sense, with the molecular magnitude, this possibility having been fore-

seen through our studies of inulin and starch. The optical effect of methylation is also consistent with previous experience, but the essential fact which emerges from the results given in the table is that mono- and di-glucosan are unique members of the series. The former gives rise to only one methylated sugar (2 : 3 : 5-trimethyl glucose) and the latter yields a mixture from which trimethyl glucose is absent. Thereafter, in the higher polymerides, 2 : 3 : 5-trimethyl glucose is again encountered as an end-product and, in the case of the mixed polyglucosans, this sugar is present in equimolecular proportion with the higher and lower homologues. This represents an average result, to which all polymerides higher than diglucosan have contributed, and the discussion can therefore be focussed on the three types represented by (*a*) mono-, (*b*) di-, and (*c*) poly-glucosan.

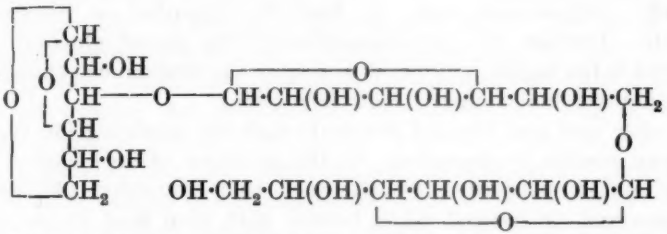
Mechanism of the Polymerisation.

The initial step of the polymerisation can be traced from the significant fact that 2 : 3 : 5 : 6-tetramethyl glucose and a dimethyl glucose are invariable products from all the polyglucosans. It follows that the first action is the conversion of glucosan into glucose, one molecule of which condenses with a second molecule of glucosan so that, once the process is initiated, it is catalytically continued. The experimental conditions employed in the polymerisation are favourable to this cycle of reactions, and no other explanation seems possible. If this be correct, the dimeride should differ from the monomeric parent in having the hydroxyl groups unequally distributed in the ratio of four in one glucose residue to two in the other. The results obtained show that this consideration applies quantitatively. The precise way in which glucose condenses with a molecule of glucosan must nevertheless remain unknown until the constitution of the dimethyl glucose isolated from diglucosan has been established, and, despite laborious investigation, this has not been solved. As shown in the experimental part, however, the sugar must be either 2 : 3- or 2 : 5-dimethyl glucose and, as the latter alternative is more strongly supported, it is provisionally adopted, leading to the following structure for diglucosan:



A. Glucosan residue. B. Glucose residue.

Speculation on the next stage of the polymerisation is guided by the fact that all polymerides above diglucosan give 2 : 3 : 5-trimethyl glucose. This can originate only from the molecular fragment B and not from A as, otherwise, the methylated sugars obtained from triglucosan would be two molecules of tetramethyl glucose and one molecule of monomethyl glucose. The attachment of the third glucose residue is thus definitely restricted to position 6 of residue B, giving the following constitution for triglucosan :



As the yields of methylated sugars from tetra- and hepta-glucosan have no quantitative significance, it is inadvisable to discuss the further steps involved in the polymerisation, but the examination of the mixed polyglucosans contributed valuable information. On occasions, these higher glucosans formed as much as 75% of the total material polymerised, so that they may be regarded as representative of the whole reaction. Inspection of the experimental details will show that this material not only gives the three methylated sugars required by the above formula, but does so in precisely equimolecular proportions. This result has been verified on more than one occasion; it cannot be regarded as adventitious and it disposes of the possibility that the trimethyl glucose originates in a simple polymeride of glucosan in which the molecular constitution of the parent molecule is preserved. It is, nevertheless, conceivable that molecules of monomeric glucosan may become associated, either together or with simple polymerides, and the existence of such compounds as hepta- and octa-glucosan indicates that this should not be ruled out. Further, the tetraglucosan examined by Pringsheim yielded no trimethyl glucose, but gave rise to the same sugars as we have now shown to originate from diglucosan. Taking a general survey of the results, it is clear that the polymerisation involves reactions of two types: one involving association and the other condensation. For example, when diglucosan is formed it may either condense with an additional molecule of glucosan to give the trimeride which, in turn, by further condensation yields a tetrameride, or alternatively, two dimeride molecules may become associated to give an entirely

different type of tetraglucosan. The inclusion of Pringsheim's results with our own renders this view more than speculative and a similar complexity may accompany each stage of the polymerisation. Our results do not provide conclusive evidence on this point and reveal only the primary nature of the polymerisation. It is of special interest to note that two-thirds of the triglucosan formula consists of a residue present in the accepted formula for maltose, a remarkable similarity in structure considering the drastic conditions employed in the preparation of the trimeride. Triglucosan may, in fact, be regarded as *glucosan maltoside*. Further, the β-configuration of the parent glucosan is preserved in the higher polymerides, despite the pronounced changes in rotation which accompany their formation.

The view now put forward demands that the condensation type of polymerisation is dependent on the presence of free hydroxyl groups, and is supported by the fact that trimethyl glucosan was recovered unchanged when heated with zinc dust in an exhausted sealed tube at 250° for 10 hours. Under similar conditions the use of zinc chloride as a catalyst resulted in profound decomposition, but, on limiting the reaction to 3 hours at 160°, the rotation altered from lævo to dextro owing to conversion of the glucosan into trimethyl glucosidotrimethyl glucose.

Applicability of the Methylation Process to the Structural Problems of Carbohydrates.

The criticism has been put forward that our method of determining the structure of carbohydrates, although diagnostic in the case of simple sugars, may not be applicable to the "closed-chain structures" represented by polysaccharides and similar compounds. It is difficult, in view of the mass of consistent results obtained with many types of non-reducing carbohydrates, to find any justification for this objection; but as at present much reliance is placed on the validity of the methylation process as a means of determining constitution, the occasion is opportune to take into account the essential requirements of the method.

The principles developed in this laboratory can be applied to the structural problems of carbohydrates, provided the following primary conditions are satisfied: (1) that methylation does not alter the configuration of a sugar; (2) that methylation does not disturb the positions in which sugar residues are attached to each other, or to other groups; and (3) that, under the conditions employed in methylation and in hydrolysis, non-glucosidic methoxyl groups do not migrate from one position to another in a sugar chain. In default of direct experimental evidence to the contrary,

and in view of the following observations, it may be claimed that the above requirements are satisfied. According to circumstances, the methylation of carbohydrates, as practised by us, is effected either by the silver oxide reaction or by the methyl sulphate method, used independently or in succession. It has been adequately proved that these alternative methods, when applied to the same compounds, give the same methylated sugars, the only distinction being that the alkaline reagent acts upon reducing sugars to give a larger excess of the corresponding β-glucoside. Configuration is therefore affected, but only so far as the reducing group is concerned. The one aspect of configuration, however, which is utilised in our deductions is that of the non-reducing groups, and it has long been known that the silver oxide reaction yields derivatives which retain the configuration of the parent compound. The conversion of *d*-dimethoxysuccinic acid into *d*-tartaric acid (Purdie and Barbour, J., 1901, **79**, 972) is a convincing, but by no means unique, example of this regularity. In addition, mono-, di-, tri-, and tetra-methyl glucose, all of which were prepared by the silver oxide reaction, have been demethylated and converted into glucose phenylosazone showing the correct optical activity.

That the second and third requirements of the method are fulfilled is shown in numerous ways. For example, Haworth and Leitch subjected maltose and cellobiose to identically the same methylating treatment, yet isolated isomeric trimethyl glucoses in the two investigations. This result cannot be reconciled with the idea that molecular linkages are altered by methylation or that the methyl groups fail to retain their positions. The evidence is equally clear in the case of the more unstable types of carbohydrate derivatives such as γ-glucosides and the existence of isomeric tetramethyl glucoses and of the corresponding tetramethyl fructoses, which reflect accurately the essential properties of the compounds from which they are derived, may be quoted in illustration. In this connexion, it is important to note that with the exception of the glucosidic alkyl group (which, in any case, is not concerned with our structural studies) the stability towards acids and alkalis of the methyl groups in a sugar chain is remarkable. Concentrated sodium hydroxide at the boiling point has no effect on a fully methylated hexose and, in our experience, the elimination of the methyl groups from an alkylated reducing sugar has been accomplished only by such processes as boiling with concentrated hydriodic acid, heating under pressure with glacial acetic acid saturated with hydrogen bromide, or, in one example,* by prolonged action with

* This result, which is unpublished, was obtained with a dimethyl galactose which yielded a monomethyl galactosazone. A similar irregularity is reported

the phenylosazone reagents. This stability is far removed from that encountered in cases where methyl groups have been shown to migrate or to enter an irregular position (see Kubota and Perkin, this vol., p. 1889).

It is possible that the frequency with which 2 : 3 : 6-trimethyl glucose has been obtained from different polysaccharides may have suggested the idea that the reagents had converted definitely isomeric compounds into a common form so that the same sugar would inevitably be produced in all cases. The results of the present investigation go far to refute this remote possibility. The only practical distinction between the alkylation of a polysaccharide and that of a simple sugar is that, owing to solubility difficulties and to steric hindrance, it is necessary in the former case to use the methyl sulphate method throughout and to repeat the methylation many times. This treatment may conceivably affect the degree of polymerisation of a compound, but as the discussion does not involve this point it may be focussed on the question if the repeated use of the alkaline reagent gives results divergent from those obtained by restricted treatment with silver oxide and methyl iodide. For this purpose, we have selected β-glucosan as a test substance and, after ten methylations by means of methyl sulphate, obtained a normal yield of the same crystalline trimethyl glucosan formerly prepared by the alternative method (Irvine and Oldham, *loc. cit.*). On extending the process until a total of twenty treatments had been given, the same product was again obtained. The result shows that even when the methyl sulphate process is repeated as often as in the case of cellulose, starch, and glycogen, the methyl groups enter the same positions in glucosan as they do when the silver oxide reaction is used only once, and, further,

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by Freudenberg and Hixon (*Ber.*, 1923, **56**, 2119) and confirmed by Levene and Meyer (*J. Biol. Chem.*, 1924, **59**, i, 145), who found that a monomethyl mannosediacetone was completely hydrolysed by treatment with very dilute acid, a property which indicates that the compound was a γ-methylmannoside diacetone. Should this prove to be the case, rearrangement may have taken place between a methyl group and an *iso*propylidene group during either methylation or hydrolysis. Numerous examples are now known of the reversible displacement of *iso*propylidene and methyl, but the reaction proceeds in acid solution, whereas Freudenberg's process does not admit of this condition. Apparently the configuration of mannose is conducive to irregular results. It may be recalled (Irvine and Paterson, J., 1914, **105**, 915) that one hydroxyl group in mannitol resists methylation completely and that, when methylglucosamine (α-amino-methylmannoside) is acted upon by dilute nitrous acid, not only is the amino-group removed, but the methyl group, which is otherwise remarkably stable, also is eliminated. In consequence, the alkylated mannoses have not been applied by us to structural studies.

that alkyl groups show no tendency to migrate to the 2 : 3 : 6-positions. The dextrins described in the present paper were also subjected to repeated methylation, yet the sugar finally obtained consisted exclusively of 2 : 3 : 5-trimethyl glucose and no trace of the 2 : 3 : 6-isomeride was detected. Precisely the converse applies when cellulose is subjected to parallel treatment, as 2 : 3 : 6-trimethyl glucose alone constitutes the final product. It is difficult to imagine that these sharply differentiated results, obtained under duplicate conditions, are due to the vagaries of the reagents rather than to inherent structural differences in the parent compounds.

Clearly, however, the silver oxide reaction when applied to polymerides tends to lower the degree of polymerisation, as indicated by a change in solubility and an alteration of the rotatory power in the direction of that of the parent unit. This phenomenon has already been encountered in the investigation of methylated inulin and has again been observed when, for comparative purposes, the mixture of higher polyglucosans was subjected to this reaction.

Experimental.

Polymerisation of β-Glucosan.—As the polymerisation of β-glucosan gives rise to a variety of isomerides, it is necessary to specify accurately the experimental method adopted in preparing the polymerides now described. In the first series of preparations, small quantities (7 g.) of glucosan were used in each experiment and this weight of material, together with 0·1 g. of zinc dust, was introduced into a 300 c.c. distilling flask, the neck of which was sealed by a cork carrying a manometer. To the side limb a T-tube was attached, provided on one branch with a tap (A) leading to the water pump and, on the other, with two taps (B and C). These were placed closely together so that the enclosed volume was small, C being connected to a supply of pure dry hydrogen. The flask, which with the exception of the side fittings was immersed in an asbestos air-bath provided with windows, was exhausted, and the residual air washed out with hydrogen. After again evacuating, the temperature of the bath was raised to 250°, the tap A being closed when the glucosan began to melt, as otherwise the compound volatilised unchanged. After about 15 minutes the melt became viscous and, as frothing ensued, the tap A was opened at intervals. In approximately 30 minutes from the start of the reaction, the frothing usually became most severe and it was then necessary to close A and C, and open B momentarily. A bubble of hydrogen was thus introduced which served to break the film of glucosan, and thereafter both C and A were rapidly opened and closed. In from 60 to 75 minutes from the time the glucosan was thoroughly melted,

frothing became sluggish and, unless A remained open for a considerable time, ceased entirely. At this stage, heating was stopped and the flask allowed to cool, the vacuum being maintained. No loss of weight was recorded under the above conditions and no charring took place.

Direct Isolation of Polyglucosans.

The product of several preparations was extracted with the minimum quantity of hot water and, on the addition of rectified spirit to the united solutions, a dark-coloured precipitate was formed. This was removed and absolute alcohol added to the filtrate. The dextrin then separated as a fine powder except in cases where too much water was present, when a sticky precipitate was produced. In such an event the liquid was decanted, the residue dissolved in a small quantity of warm water and, after removal of the solvent, dried at 100°/15 mm.; the product could then be readily powdered. The less-soluble dextrin obtained as above is referred to as "Dextrin I." The mother-liquor which had deposited Dextrin I was concentrated and the addition of alcohol repeated until no further precipitate was formed. In this way the material was separated into two further portions (Dextrins II and III), each fraction being relegated to its class on the basis of solubility and specific rotation.

Examination of Dextrin I. Heptaglucosan.—The material was redissolved in hot water and boiled with charcoal, a treatment which removed colouring matter and also diminished the yield considerably. Finally, the compound was precipitated with alcohol and dried in a vacuum. *Dextrin* I was thus obtained as a slightly hygroscopic powder which, although perfectly white, gave a pale yellow solution in water. Analysis of different preparations gave C, 44·5, 44·45; H, 6·4, 6·2; ash, 0·266 ($C_6H_{10}O_5$ requires C, 44·4; H, 6·2%). Dextrin I is insoluble in organic solvents, with the exception of acetic acid, but is freely soluble in water, giving a non-reducing dextrorotatory solution. $[\alpha]_D + 83·9°$ for $c = 2·08$. This value was obtained in different preparations and when a specimen of the material was fractionally precipitated with alcohol the most active fraction showed $[\alpha]_D + 85·8°$, thus indicating the uniformity of the compound. Despite this observation and the fact that dextrin I was afterwards shown to be heptaglucosan, the application of Karrer's method of determining the molecular magnitude of polymerised units by analysis of the sodium hydroxide compounds gave inconclusive results which lay between those required for $(C_6H_{10}O_5)_3$ and $(C_6H_{10}O_5)_4$.

For analytical and reference purposes the *triacetate* was prepared

by boiling the dextrin, until dissolved, with excess of acetic anhydride containing zinc chloride. The product was isolated by precipitation with water, washing with ether and solution in a large excess of hot absolute alcohol, from which it separated as a fine, white powder. After three such treatments, the m. p. was constant (142°) (Found : C, 49·95; H, 5·6; $CH_3 \cdot CO_2H$, 65·6. $C_{12}H_{16}O_8$ requires C, 50·0; H, 5·55; $CH_3 \cdot CO_2H$, 62·5%). The triacetate is insoluble in water, cold absolute alcohol, or ether, soluble in other organic solvents including aqueous alcohol. $[\alpha]_D$ in 50% alcohol + 85·1° for $c = 2{\cdot}2315$.

When heated for 2 hours at 70° in methyl alcohol which was nearly saturated with hydrogen chloride, the dextrin was completely converted into methylglucoside. Initially excess of β-methylglucoside was formed, but, on continuing the reaction for $2\frac{1}{2}$ hours, the equilibrium mixture was obtained, from which pure α-methylglucoside was isolated in the usual manner (m. p. 164°; OMe, 15·1%; $[\alpha]_D$ in water + 158·4°).

Examination of Dextrin II. Tetraglucosan.—This substance was produced in greatest yield when the polymerisation of β-glucosan was carried out in quantities of 20 g. at a time, a 600 c.c. flask being employed. The subsequent procedure was as described, and after removal of dextrin I, the more soluble products were fractionally precipitated with alcohol. Fractions showing similar rotatory power were mixed and again precipitated so that, by prolonged repetition of this process, the total product was ultimately separated into two portions which could not be further sub-divided. These showed, respectively, $[\alpha]_D$ + 60·7° and + 29·9° in aqueous solution and are indexed as *dextrin* II and *dextrin* III. Both substances were fine, white, hygroscopic powders and had the same composition as the parent glucosan. Dextrin II, when acetylated as already described, gave the same triacetate as dextrin I (Found : C, 50·2; H, 5·6; $CH_3 \cdot CO_2H$, 63·6%). The specific rotation and melting point also agreed within experimental error, and, on hydrolysing the acetate with sodium hydroxide, dextrin I was regenerated (Found : C, 44·5; H, 6·1; $[\alpha]_D$ + 81·5° for $c = 2{\cdot}14$ in water. Dextrin I requires C, 44·4; H, 6·2%; $[\alpha]_D$ + 83·9° for $c = 2{\cdot}08$).

Dextrin II was readily converted into methylglucoside. The solid was covered with methyl alcohol, and hydrogen chloride passed in from time to time until the dextrin dissolved, after which the solution was diluted with more alcohol and heated at 70°, polarimetric readings being taken every 15 minutes. In one hour the constant value $[\alpha]_D$ + 94·5° (calc. on the weight of glucoside formed) was reached and the product was then isolated as usual.

A crystalline mixture of α- and β-methylglucosides was thus obtained from which the pure α-form was separated by crystallisation from alcohol (Found: m. p. 165—166°; $[\alpha]_D$ + 157·2°; OMe, 15·6. α-Methylglucoside requires m. p. 165—166°; $[\alpha]_D$ + 157·5°; OMe, 15·9%).

When the above reaction was conducted at 50°, in place of 70°, and was arrested after 45 minutes, β-methylglucoside was the chief product and the α-form was present only to the extent of 20%.

Examination of Dextrin III. Triglucosan.—In all respects, save solubility and specific rotation, dextrin III resembled dextrin II. Like the latter, it yielded apparently the same triacetate as dextrin I (Found: C, 50·1; H, 5·6; $CH_3 \cdot CO_2H$, 62·3%). The specific rotation in aqueous alcohol was, however, + 74·2° in place of 78·9°, but this discrepancy appears to be due to a trace of impurity, as, on treatment with sodium hydroxide, dextrin I was regenerated. Dextrin III was also converted into methylglucoside in the usual way. The total crystalline product isolated showed $[\alpha]_D$ + 92·9° for $c = 1$ in methyl alcohol, and gave OMe, 15·3%. On crystallisation from absolute alcohol, pure α-methylglucoside displaying the standard constants was obtained. In this case also, when the reaction was restricted to heating at 50° for 1 hour, β-methylglucoside was the chief product.

Methylation of the Individual Dextrins.

As the methods adopted for the methylations have been described in previous papers from this laboratory, only significant results are now quoted.

Methylation of Dextrin I. Heptaglucosan.—The action of silver oxide and methyl iodide on a methyl-alcoholic solution was definitely arrested at the stage where two alkyl groups had been introduced per C_6 unit. Product: a colourless glass, easily powdered. $[\alpha]_D$ in chloroform + 76·0° for $c = 0·6035$ (Found: C, 50·65; H, 7·4; OMe, 32·4. $C_8H_{14}O_5$ requires C, 50·5; H, 7·4; OMe, 32·6%). The methyl sulphate reaction was more effective, repeated treatment with the reagents under conditions similar to those employed with inulin giving a product readily soluble in organic solvents and showing $[\alpha]_D$ in chloroform + 89·4° for $c = 2·745$. The methylation was, however, still incomplete, but approximated to the trimethyl stage [Found: C, 53·0; H, 7·5; OMe, 40·9. $(C_9H_{16}O_5)_n$ requires C, 52·9; H, 7·8; OMe, 45·5%]. No further purification was possible, as the compound, which was isolated as a glass readily convertible into a white powder, was exceedingly soluble in organic solvents with the exception of light petroleum. The molecular

weight, determined in benzene by the cryoscopic method, was 1446, whereas a hepta (trimethyl glucosan), $C_{63}H_{112}O_{35}$, requires 1428.

As, contrary to expectation, methyl alcohol containing 1% of hydrogen chloride proved to be without action on the compound, simultaneous hydrolysis and condensation was effected by heating for 15 hours at 70° with alcohol nearly saturated with the gas. No charring resulted from this drastic treatment and the specific rotation showed the usual characteristic rise and fall during the change. ($[\alpha]_D + 75{\cdot}0° \rightarrow 93{\cdot}7° \rightarrow 87{\cdot}5°$). The mixed glucosides were isolated by vacuum distillation as a colourless syrup (OMe, 50·4%) and were hydrolysed thereafter by means of 3% aqueous hydrochloric acid to give a solution of methylated glucoses showing $[\alpha]_D + 68{\cdot}4°$. A syrup was finally obtained on distillation showing OMe, 38·6% and yielding crystalline tetramethyl glucose on extraction with boiling light petroleum. The remaining sugars were di- and tri-methyl glucoses in unknown proportions.

Methylation of Dextrin II. Tetraglucosan.—As a result of three methylations by the methyl sulphate method, 18 g. of the dextrin were converted into 16·5 g. of a viscid syrup showing $[\alpha]_D + 66{\cdot}6°$ for $c = 3{\cdot}3335$ in chloroform, and having OMe, 39·5%. Two further methylations raised the methoxyl content to 41·6%, and four subsequent treatments gave the maximum value of 43·4%. The product was a glass possessing the customary solubilities [Found: C, 53·0; H, 7·8; OMe, 43·4. $(C_9H_{16}O_5)_n$ requires C, 52·9; H, 7·8; OMe, 45·5%].

Solvent.	c.	$[\alpha]_D$.
Methyl alcohol	1·3625	+68·7°
Acetone	1·958	70·5
Chloroform	2·900	61·2

Molecular weight, determined by the cryoscopic method in benzene solution, = 873. Tetra (trimethyl glucosan), $C_{36}H_{64}O_{20}$, requires 816.

When converted into the corresponding methylglucosides, as described in the case of the hepta-isomeride, the product on distillation showed in successive experiments OMe, 49·6, 49·7% and $[\alpha]_D + 100{\cdot}9°$ in water for $c = 1{\cdot}3016$. On hydrolysis with 4% aqueous hydrochloric acid the permanent value for the specific rotation was + 66·7°. The mixture of sugars thus obtained had OMe, 38·9% and was separated into (*a*) a fraction, soluble in ether, amounting to about two-thirds of the total, and (*b*) a fraction, consisting of the remainder, soluble in acetone but not in ether. From the soluble portion, tetramethyl glucose crystallised spontaneously and was identified by analysis and by determination of the physical constants. The uncrystallisable sugars were mixed,

converted into their methylglucosides, distilled in three fractions, and analysed. The methoxyl contents, in order of increasing volatility, were respectively 38·3, 44·8, and 53·4%, showing that the compounds were derived from a di- and a tri-methyl glucose. In no case did any of the sugars give a phenylosazone and the incompletely methylated forms were convertible into the stable variety of tetramethyl glucose in 80% yields.

It was necessary to ensure that the tetramethyl glucose isolated did not originate in degradation during the methylation of the original dextrin. The methylated dextrin was therefore extracted repeatedly with boiling light petroleum, but this did not cause any alteration in the methoxyl content. Further, when heated at 200°/0·2 mm., the methylated dextrin distilled very slowly, but analysis of the distillate showed that no tetramethyl methylglucoside was present.

Methylation of Dextrin III. Triglucosan.—Twenty grams, subjected to eleven successive treatments by the methyl sulphate reaction, gave 15·3 g. of a colourless glass convertible into a white solid [Found: C, 52·7; H, 7·8; OMe, 42·2. $(C_9H_{16}O_5)_n$ requires C, 52·9; H, 7·8; OMe, 45·5%].

Solvent.	*c.*	$[\alpha]_D$.
Chloroform	2·1035	+53·5°
Acetone	2·048	56·4
Methyl alcohol	1·753	52·8

The molecular weight, determined by the cryoscopic method in benzene, was 595. Tri(trimethyl glucosan), $C_{27}H_{48}O_{15}$, requires 612. When heated in a vacuum, approximately one-half of the material distilled at 180—200°/0·5 mm., but this result was evidently due to depolymerisation, as the distillate was a comparatively mobile syrup having $n_D = 1·4770$ and $[\alpha]_D$ in chloroform + 23·9°. The composition remained unaltered (OMe, 44·7%). The methylated dextrin, when subjected to the joint action of methyl alcohol and hydrogen chloride, was converted into the corresponding mixture of alkylated methylglucosides, the whole of the product being distillable, although over a wide temperature range. No fractionation was attempted, the total distillate being hydrolysed in one experiment by boiling with 4% aqueous hydrochloric acid. It is significant that when hydrolysis was complete the corrected specific rotation of the solution was + 65·3°, showing that the end products were the same as those obtained from the hepta- and tetra-isomerides. As before, the sugars thus obtained were divided into (*a*) a fraction soluble in ether which yielded crystalline tetramethyl glucose and a trimethyl glucose, and (*b*) a fraction soluble in acetone, but not in ether. The less soluble sugar, which was purified by dissolving

in chloroform and precipitating with ether, possessed the composition of a dimethyl glucose (OMe, 33·4%), but could not be obtained in a crystalline form and failed to give a phenylosazone. Both the di- and the tri-methyl glucose formed above belonged to the butylene-oxide series and polarimetric tests for the presence of γ-forms gave negative results.

Indirect Isolation of Polyglucosans in the Form of the Methylated Derivatives.

In place of separating the polyglucosans by precipitation and conducting the methylations in different experiments, an alternative is to alkylate the total polymerised material and thereafter to separate the methylated products. The latter method proved to be more effective, more economical, and more decisive.

Thirty grams of glucosan were polymerised, as described, in each experiment. By extraction of the product with boiling rectified spirit it was possible to remove unchanged glucosan together with the bulk of the dextrins of low molecular weight, leaving polymerides of high molecular weight undissolved, and, in this way, it was shown that both types of dextrin yielded normal triacetates. It was, however, preferable to methylate the total product directly, the methyl sulphate method being used throughout. A comparatively mobile syrup was thus obtained in good yield, 80 g. of glucosan giving 73 g. of methylated polymeride. On distillation at the Gaede pump, the product was separable as under :

Fraction I.	B. p. 135°/0·2 mm.	28 grams.	Trimethyl glucosan.
Fraction II.	B. p. 205—210°/0·2 mm.	17·1 grams.	Di(trimethyl glucosan).
Residue.		27·2 grams.	Poly(trimethyl glucosan).

In a second preparation, where more complete polymerisation was effected and where over-heating during distillation was avoided, 60 g. of glucosan yielded 55 g. of methylated product which in turn gave :

Trimethyl glucosan	9·41 grams	17%
Di(trimethyl glucosan)	12·98 ,,	23·6%
Poly(trimethyl glucosan)	31·77 ,,	57·8%

The monomeric trimethyl glucosan crystallised in the receiver; the dimeride was a pale yellow, clear, viscous syrup (n_D 1·4720), whilst the undistillable isomerides consisted of a glass.

Di(trimethyl glucosan).—The composition and physical constants of the distilled syrup showed very little variation in successive preparations [Found : C, 53·0, 52·9; H, 7·7, 7·9; OMe, 44·5; *M*, cryoscopic in benzene, 418. $(C_9H_{16}O_5)_2$ requires C, 52·9; H, 7·8; OMe, 45·6%; *M*, 408].

Solvent.	*c.*	$[\alpha]_D^{20°}$.
Chloroform	1·9515	+46·5°
Methyl alcohol	1·8790	48·3
Acetone	2·0040	51·8

Conversion into methylated methylglucosides. This reaction was accomplished by boiling with methyl alcohol nearly saturated with hydrogen chloride, the specific rotation, corrected for the change of concentration, becoming constant at + 110·0°. The mixed glucosides were isolated by distillation and although the liquid boiled over a wide range of temperature the product was collected as a single fraction (yield, 97%; n_D 1·4587). Under these conditions the distillate should have the same composition as trimethyl methylglucoside and this was the case (Found: C, 50·8; H, 8·5; OMe, 51·2. $C_{10}H_{20}O_6$ requires C, 50·8; H, 8·5; OMe, 52·5%). Separation of the constituents was effected by dissolving in water containing sodium bicarbonate and extracting repeatedly with chloroform. This treatment removed all glucosides containing four or more methoxyl groups per C_6 unit, lower methylated compounds remaining in the aqueous layer. The process can be applied quantitatively and, as in the present case yields are of special importance, the results of one exact experiment are quoted. 8·5483 Grams of di(trimethyl glucosan) gave 4·9161 g. of methylated glucosides extractable with chloroform, and 3·5824 g. were retained in the aqueous layer. The less soluble compound, when isolated, dissolved in ether, dried, and recovered, proved to be dimethyl methylglucoside showing $[\alpha]_D$ + 108·4° in methyl alcohol, and n_D 1·4743 (Found: C, 48·7; H, 8·2; OMe, 41·2. Calc. for $C_9H_{18}O_6$, C, 48·8; H, 8·1; OMe, 41·8%).

Analysis of the syrup extracted with chloroform having shown that it consisted essentially of tetramethyl methylglucoside together with a little trimethyl methylglucoside, the mixture was hydrolysed to give the corresponding sugars. On repeating the extraction with chloroform, only tetramethyl glucose passed into the lower layer, whilst trimethyl glucose was retained in the aqueous layer. The tetramethyl glucose, when recovered, purified by distillation and recrystallised as usual, displayed the correct melting point and rotation (Found: C, 50·8; H, 8·4; OMe, 52·0. Calc. for $C_{10}H_{20}O_6$, C, 50·8; H, 8·5; OMe, 52·5%). In this way, 3·2457 g. of pure sugar were obtained from 4·4717 g. of the mixed glucosides. The small amount of trimethyl glucose isolated shows that this sugar cannot be regarded as a definite molecular product but originates in unpolymerised trimethyl glucosan. Neglecting this by-product and small undistilled residues, the relative yields of the hydrolysis sugars, calculated as the corresponding glucosides, become:

	Found.	Calc. for equal molecules.
Dimethyl methylglucoside	46·6	47·1%
Tetramethyl methylglucoside	53·4	52·9%

Examination of Methylated Polyglucosans.—The non-volatile residue left when di(trimethyl glucosan) was separated by distillation constituted the main product of the methylation of polymerised glucosan. After solution in ether, filtration and removal of the solvent, the mixture of higher polymerides was obtained as a clear glass. The carbon content was low, although the composition was uniform in different preparations [Found: C, 52·4, 52·4; H, 7·6, 7·8; OMe, 44·4, 45·2. $(C_9H_{16}O_5)_n$ requires C, 52·9; H, 7·8; OMe, 45·5%]. As, from its method of preparation, the material consisted of all polymerides higher than the dimeride, no molecular weights were determined.

Solvent.	*c.*	$[\alpha]_D$.
Chloroform	1·850	+63·3°
Acetone	2·266	66·6
Methyl alcohol	1·755	64·4

Conversion by the action of acid methyl alcohol into the mixture of methylated glucosides gave a 95% yield of a colourless syrup, which was distilled under 0·4 mm. and collected in one portion without fractionation. The average composition of the total distillate should be the same as that of trimethyl methylglucoside, but although this held approximately, all the values were low (Found: C, 50·4; H, 8·3; OMe, 50·6. Calc. for $C_{10}H_{20}O_6$, C, 50·9; H, 8·5; OMe, 52·5%). On separating the constituent glucosides by extraction of an aqueous solution containing sodium bicarbonate with chloroform, the syrup recovered from the extract weighed 69% of the original total, and the remaining 31% was recovered from the water. The former was hydrolysed with 8% hydrochloric acid to give the corresponding methylated glucoses, which were isolated in 94% yield. Analysis of the distilled sugars showed that tri- and tetramethyl glucose were present in equimolecular proportions (Found: C, 49·9; H, 8·2; OMe, 46·8. Calc., C, 49·8; H, 8·3; OMe, 47·3%). Separation of the sugars was effected by the method of chloroform extraction, 11·176 g. of the mixture giving 5·300 g. of crystalline tetramethyl glucose displaying the correct analytical figures and constants. The less soluble sugar was recovered from the water, distilled as a viscid syrup and identified as a trimethyl glucose (Found: C, 48·6; H, 7·95; OMe, 41·4. Calc. for $C_9H_{18}O_6$, C, 48·6; H, 8·1; OMe, 41·8%). The specific rotation in chloroform solution was + 72·5° but, in order to identify it completely, the sugar was converted successively into the diacetate, the monoacetobromo-derivative, and finally into the corresponding trimethyl β-methylglucoside. These steps were controlled by blank experiments in which authentic 2 : 3 : 5-trimethyl glucose was used, and the optical changes were parallel throughout. On nucleation with

2 : 3 : 5-trimethyl β-methylglucoside, the product crystallised and was purified as usual from light petroleum. The m. p., refractive index and specific rotation in methyl alcohol were correct (Found: C, 50·7; H, 8·5; OMe, 51·9. Calc. for $C_{10}H_{20}O_6$, C, 50·8; H, 8·5; OMe, 52·5%). The combined results show that the sugars extractable by chloroform from aqueous solution are 2 : 3 : 5 : 6-tetramethyl glucose and 2 : 3 : 5-trimethyl glucose in equimolecular proportion.

The lower methylated glucoside retained in aqueous solution after extraction of the tetra- and tri-methyl methylglucosides with chloroform consisted of a viscid syrup (n_D 1·4779, $[\alpha]_D$ in methyl alcohol + 106·2°). Although with material of this nature vacuum distillation is difficult, this purification was undertaken to obtain more accurate analytical figures. Pure dimethyl methylglucoside was thus obtained as the main fraction (b. p. over 190°/0·4 mm.; n_D 1·4743) (Found: C, 48·55; H, 8·2; OMe, 40·8. Dimethyl methylglucoside, $C_9H_{18}O_6$, requires C, 48·6; H, 8·1; OMe, 41·8%). The undistillable residue was a glass and consisted essentially of monomethyl methylglucoside (Found: C, 45·7; H, 7·2; OMe, 28·9. Calc. for $C_8H_{16}O_6$, C, 46·15; H, 7·7; OMe, 29·8%). About 5% of the total sugars formed from the dextrin consisted of this material, which almost certainly originates in incomplete methylation.

Attempts to establish the constitution of the dimethyl glucose isolated in the present section of the research led to no final conclusions. The sugar failed to crystallise and formed no phenylosazone; it also failed to enter into condensation with acetone when dissolved in this reagent containing 0·2% of hydrogen chloride, but reacted when the concentration of acid was raised to 1·3%. No definite benzylidene derivative could be prepared, either from the sugar or from its methylglucoside, but the combined results, although not conclusive, favour the view that of the two alternatives, 2 : 3- or 2 : 5-dimethyl glucose, the latter is more probable.

We desire to express our indebtedness to the Department of Scientific and Industrial Research for a Research Assistantship granted to one of us.

UNITED COLLEGE OF ST. SALVATOR AND ST. LEONARD,
UNIVERSITY OF ST. ANDREWS. [*Received, October 16th,* 1925.]

CCCCV.—*The Electrical Conductivities of Hydrogen Chloride and Potassium Chloride in Water and Acetone–Water Mixtures.*

By Thomas Kerfoot Brownson and Frank Maurice Cray.

The electrical conductivities of a large number of salts in acetone-water mixtures have been measured, especially by Jones and his co-workers (Jones, Bingham, and McMaster, *Z. physikal. Chem.*, 1906, **57**, 193, 257; Jones and Mahin, *Carnegie Institute of Washington Publication*, 1913, **180**, 193).

The present investigation of the electrical conductivities of hydrogen chloride and potassium chloride in water and acetone–water mixtures was carried out to obtain information in connexion with a research upon the preparation of solutions of standard hydrogen-ion concentration and the measurement of indicator ranges in an acetone–water mixture containing 10% by volume of water (Cray and Westrip, *Trans. Faraday Soc.*, 1925, **21**). Owing to the nature of the investigation, it was necessary to obtain a high order of accuracy.

A detailed survey has been made of the alteration in the electrical conductivities and the degree of dissociation of these electrolytes over a wide range of dilutions in solvents ranging from pure water to the acetone–water mixture containing only 5 volumes of water in 100 volumes of the mixed solvent. Conductivity measurements have been made for hydrogen chloride in water and eight mixtures of acetone–water and for potassium chloride in water and six acetone–water mixtures at 20° and 25° and at dilutions ranging from 10 to 10,000 litres per gram-molecule.

Experimental.

Materials.—Acetone was dehydrated over fused calcium chloride and distilled fractionally at least twice immediately before use, care being taken to avoid contamination from the air. The acetone distilled between 56·2° and 56·3° at 760 mm., and none with a specific conductivity greater than $0{\cdot}5 \times 10^{-7}$ mho. at 20° was used. This acetone compares favourably with that obtained by other investigators (*e.g.*, Dutoit and Levier, *J. Chim. Phys.*, 1905, **3**, 435; κ $0{\cdot}5$—$2{\cdot}0 \times 10^{-7}$ mho. at 20°. Benz, Dissertation, Lausanne, 1905; κ $0{\cdot}22 \times 10^{-7}$ mho. at 18°).

The water was prepared from high grade distilled water by a double distillation and had a specific conductivity less than $1{\cdot}2 \times 10^{-6}$ mho at 20°.

The hydrochloric acid was prepared in normal solution and its strength determined gravimetrically from time to time.

The potassium chloride (A.R. quality) was recrystallised three times from conductivity water, heated for some hours at 120°, and kept in a vacuum desiccator. Standard solutions were made up as required by direct weighing and standardised against silver nitrate.

Preparation of Solutions.—All mixtures of acetone and water were made up to contain the specified volume of water in 100 volumes of the mixed solvent, the final volume adjustment being carried out at 15°. Great care was paid to this dilution on account of the considerable contraction in volume (Reilly, *Proc. Roy. Dublin Soc.*, 1919, **15**, 43) and change in temperature which take place upon mixing acetone and water.

In each series of conductivity measurements, the most concentrated solution and occasionally the more dilute solutions of hydrogen chloride and potassium chloride were prepared in a manner similar to the above, the requisite volume of acid or salt solution replacing an equivalent volume of water. Subsequent dilution was carried out using specially standardised flasks and pipettes. This method was considered preferable to direct weighing on account of the volatility of the acetone.

All measurements were carried out on the same day as the solutions were made up and these were kept in the dark until actually required.

The range of dilutions covered in the case of potassium chloride was limited by its sparing solubility, especially in solvents rich in acetone. The electrical conductivities were measured at dilutions up to 10,000 litres except in solvents with a high water content; the highest dilution was then 2,500.

Apparatus.—The usual type of Kohlrausch apparatus modified as described below was used with a thermionic valve oscillator as the source of alternating current and with the telephones across the ends of the bridge wire (Schlesinger and Reed, *J. Amer. Chem. Soc.*, 1919, **41**, 1727). The bridge wire, calibrated by the method of Strouhal and Barus and of accurately measured resistance, could be extended at either end by means of non-inductive standard resistance coils. The other arms of the bridge contained a standard resistance box and the electrolytic cell respectively, whilst two variable air-condensers were arranged in parallel, so that they could be connected in parallel across either arm of the bridge as required, in order to balance the capacities in the system.

All connecting wires were of stout copper and of known resistance, which was corrected for when necessary.

The thermostats were regulated to $\pm 0{\cdot}05°$ by means of Lowry regulators with electrical control and all metal parts were earthed.

Source of Current.—Taylor and Acree (*J. Amer. Chem. Soc.*, 1916, **38**, 2415) have shown that the resistance of an electrolyte in aqueous solution measured between platinised electrodes of half-inch diameter alters with frequency up to 600 cycles, but that there is no change of resistance at high frequencies, which were investigated up to 2,000 cycles.

Preliminary work on these acetone–water mixtures with an induction coil as the source of alternating current showed that accurate reproducible results were unobtainable on account of the lowness and inconstancy of the frequency together with the unsymmetrical and irregular nature of the current. This source of current was therefore discarded in favour of a Sullivan thermionic valve oscillator, the frequency of the alternating current being readily adjustable by means of the anode condenser. The frequency used in this investigation was 1060 cycles, which was sufficiently high to reduce the possibility of polarisation in the cell and also gave a note readily detected in the telephones.

A cathode ray oscillograph was used to ascertain whether the current had a pure sinusoidal form.

No difficulty was experienced even at the highest dilutions in obtaining an excellent minimum in the telephones, when the resistances and capacities were accurately balanced.

Conductivity Cells.—Taylor and Acree (*loc. cit.*) have shown that in aqueous solution, whilst there is no change of resistance with change in frequency when platinised electrodes are used at frequencies above 600 cycles, there is a fall in resistance with increasing frequency when plain platinum electrodes are used. When these results are extrapolated to infinite frequency, the resistance measured with plain electrodes is identical with that found at the lower frequencies with platinised electrodes.

A preliminary survey of the behaviour of electrodes in acetone–water mixtures showed that the resistances of solutions measured with plain electrodes were higher than the resistances of the same solutions measured with platinised electrodes, but that the discrepancy between them decreased as the resistance of the solution being measured increased. Thus, in the acetone–water mixture containing 10% by volume of water, the results obtained at the higher dilutions with either electrode surface were substantially identical.

The possibility of error due to the catalytic action of the platinum black on the acetone was investigated in a series of experiments in which the specific conductivities of hydrogen chloride solutions

containing one gram-molecule in 20, 500 and 5,000 litres of 95 : 5 acetone–water were measured at 20° for periods up to 50 minutes, during which time the current was passing through the cell.

The maximum alteration in specific conductivity of these solutions over this period was $\pm 0{\cdot}15\%$ at the highest dilution, but as the changes were in the direction of both increased and decreased specific conductivity, any alteration was ascribed to temperature fluctuations and experimental error in determining the bridge setting.

The conclusion is drawn that the use of platinised platinum electrodes is not attended by objection in acetone–water mixtures on account of catalytic action of platinum black on the solvent.

Three cells having cell constants 0·5703, 0·4686, and 0·1686 were used for the measurement of the specific conductivities of the electrolyte solutions. The standard solution for determining these constants was 0·02*N*-aqueous potassium chloride; its specific conductivity at 25° being taken from the results of A. C. Melcher (Noyes and Falk, *J. Amer. Chem. Soc.*, 1912, **34**, 454). The cell constants were checked at frequent intervals during the course of the research and wherever possible the conductivity of a solution was measured in two cells having respectively low and high cell constants.

The cells were all of the same type, consisting of a tubular borosilicate glass vessel, closed by means of a stopper and fitted in each case with lightly platinised platinum disk electrodes, 1 cm. in diameter, mounted vertically on stout platinum leads, which were carried through the walls of the vessel into side tubes containing mercury.

Solvent Correction and Calculation of the Equivalent Conductivity at Infinite Dilution.—The corrections which should be applied to values of the specific conductivities of electrolytes on account of the conductivity of the solvent itself have been discussed by several investigators. Kendall (*J. Amer. Chem. Soc.*, 1917, **39**, 7) has summarised the position and concludes that, if the solvent is of sufficiently high degree of purity, no correction need be applied in the case of acids stronger than acetic acid throughout the ordinary range of dilution, but that where the electrolyte is the salt of a strong acid and strong base, substantially accurate values are obtained by the procedure of Kohlrausch, namely, direct subtraction of the whole of the solvent conductivity.

The dissociation constant calculated for hydrogen chloride from conductivity measurements falls as the percentage of acetone in the mixed solvent increases, but even in the solvent containing 5 volumes of water in 100 volumes of acetone–water it is approximately 6×10^{-4} at 25° compared with $1{\cdot}8 \times 10^{-5}$ at 25° for acetic

acid in water. Consequently, no correction has been applied on account of the conductivity of the solvent itself to the values obtained for hydrogen chloride in these acetone–water mixtures, but in the case of potassium chloride the whole of the solvent conductivity has been subtracted.

In all cases the specific conductivity of the solvent was small in comparison with that of the electrolytes, even at the highest dilutions.

The values for the equivalent conductivity at infinite dilution have been calculated by the method suggested by Washburn (*J. Amer. Chem. Soc.*, 1918, **40**, 122) from the equivalent conductivities at the highest dilutions measured, the value of the mass-action expression $\lambda_v^2/\lambda_\infty(\lambda_\infty - \lambda_v)v$ being plotted against the concentration for various assumed values of λ_∞ and that figure for λ_∞ being taken as the most probable which led to no abrupt rise or fall in the curve at the highest dilution.

The degree of dissociation of the electrolytes has been obtained from the expression $\alpha = \lambda_v/\lambda_\infty$, no account being taken of the change of viscosity with dilution.

Results.

The influence of variation in the composition of the solvent will be shown to be extremely marked in acetone–water mixtures of high acetone content, especially in the case of the more concentrated electrolyte solutions. Thus, alteration in the water content from 5 to 10% by volume is accompanied by a 100% change in the equivalent conductivity at dilution $v = 50$ and by a 2·5% change at $v = 10{,}000$. The measurements in all acetone–water mixtures were repeated several times with different samples of acetone. Thus, in the case of hydrogen chloride in the solvent containing 10% by volume of water, nine separate series of measurements at all dilutions were made with different samples of acetone. The results given in all cases are the mean values. In the solvent mentioned, the variation from the mean of these nine series of results over all dilutions was $\pm$ 0·5% and the reproducibility in solvents richer in water was of considerably higher degree of accuracy. In the solvent containing 50% by volume of water, the variations were only $\pm$ 0·2%, the results in the different series being in the same relative order at all dilutions.

A series of at least ten measurements with different bridge settings was made for every solution, the maximum divergence from the mean being generally less than $\pm$ 0·05%.

Owing to the considerable difficulties in obtaining really accurate values in pure acetone, due particularly to the marked effect of

TABLE I.

Equivalent conductivities of hydrogen chloride in acetone–water mixtures at 25°.

	Volume % of water								
v	5	10	20	35	50	65	80	90	100
10	—	20·89	51·49	99·44	149·7	202·1	270·1	321·3	389·9
20	13·76	—	—	—	—	—	—	—	—
25	—	30·81	63·93	110·1	158·0	211·0	281·6	332·0	401·0
50	19·70	38·93	72·88	116·9	162·7	215·9	286·8	336·0	406·4
100	26·15	48·42	80·55	122·6	167·3	219·7	290·3	341·0	411·0
250	37·50	63·40	91·40	129·0	172·5	224·3	293·3	344·2	415·3
500	48·08	73·96	96·55	132·2	174·2	225·8	295·0	346·6	418·0
1,000	60·39	83·13	100·8	133·8	175·4	226·6	296·4	348·0	419·5
2,500	77·47	93·16	104·9	135·8	175·9	227·3	297·3	348·9	420·7
5,000	88·41	98·22	106·4	137·0	176·3	227·5	—	—	—
10,000	97·61	101·5	107·7	137·7	176·5	—	—	—	—
∞	(112·2)	(105·5)	(109·1)	(138·5)	(176·8)	(227·8)	(297·9)	(349·6)	(422·0)
κ of solvent in mho × 10^{-6}	0·054	0·11	0·20	0·30	0·44	0·55	0·75	0·85	1·0

TABLE II.

The equivalent conductivities of hydrogen chloride in acetone–water mixtures at 20°.

	Volume % of water.						
v.	5.	10.	20.	35.	50.	80.	100.
10	—	19·70	47·86	90·77	135·7	247·0	362·5
20	13·21	—	—	—	—	—	—
25	—	28·77	59·02	100·4	143·1	257·6	372·5
50	18·97	36·55	67·20	106·4	147·1	262·4	376·9
100	25·05	45·37	74·24	111·7	151·1	265·1	380·6
250	35·90	59·29	84·10	117·3	155·6	267·8	384·5
500	45·88	69·00	88·60	119·9	157·1	269·4	387·2
1,000	57·54	77·28	92·35	121·3	158·1	270·4	388·1
2,500	73·55	86·50	96·10	123·0	158·6	271·3	389·5
5,000	83·80	91·25	97·25	123·7	158·9	—	—
10,000	92·56	94·40	98·40	124·5	159·1	—	—
∞	(106·4)	(98·0)	(99·7)	(125·2)	(159·3)	(272·0)	(390·6)
κ of solvent in mho × 10^{-6}	0·049	0·09	0·18	0·26	0·40	0·68	0·90

TABLE III.

The equivalent conductivities of potassium chloride in acetone–water mixtures at 25°

	Volume % of water.						
v.	5.	10.	20.	35.	50.	65.	100.
50	—	—	53·20	59·75	67·45	80·40	138·6
100	—	58·90	60·32	64·47	70·80	82·09	141·6
250	—	72·95	68·50	68·49	74·02	85·20	145·2
500	—	82·50	73·20	70·95	75·70	86·00	146·7
1,000	98·39	89·00	76·54	73·00	76·61	86·70	147·7
2,000	108·1	—	—	—	—	—	—
2,500	—	98·80	79·80	74·65	78·00	87·75	149·1
5,000	117·9	99·15	81·30	75·90	78·64	88·40	—
10,000	122·4	101·3	82·80	—	—	—	—
∞	(127·7)	(103·7)	(84·50)	(77·30)	(79·40)	(89·10)	(150·1)
κ of solvent in mho × 10^{-6}	0·054	0·11	0·20	0·30	0·44	0·55	1·0

TABLE IV.

The equivalent conductivities of potassium chloride in acetone–water mixtures at 20°.

	Volume % of water.						
v.	5.	10.	20.	35.	50.	65.	100.
50	—	—	48·81	53·81	60·00	71·27	125·5
100	—	55·05	55·20	57·81	63·02	72·78	128·2
250	—	68·13	62·60	61·39	65·80	75·28	131·0
500	—	76·40	66·85	63·60	67·10	76·05	132·1
1,000	92·31	82·28	69·91	65·42	68·01	76·70	132·9
2,000	101·5	—	—	—	—	—	—
2,500	—	88·40	72·75	66·60	69·03	77·50	134·3
5,000	110·2	91·70	74·00	67·70	69·65	78·00	—
10,000	114·3	93·60	75·30	—	—	—	—
∞	(119·1)	(95·7)	(76·90)	(68·90)	(70·3)	(78·60)	(135·2)
κ of solvent in mho × 10^{-6}	0·049	0·09	0·18	0·26	0·40	0·50	0·90

TABLE V.

The equivalent conductivities of hydrogen chloride in water at 18° *and* 25° *and of potassium chloride at* 25°.

	Hydrogen chloride.				Potassium chloride. 25°.		
	18°.		25°.				
v.	This research.	Goodwin and Haskell (interpolated).	This research.	Bray and Hunt (interpolated).	This research.	Melcher.	Lorenz (interpolated).
10	351·7	351·4	389·9	390·4	—	129·0	—
25	362·0	—	401·0	400·7	135·4	—	135·1
50	364·9	365·5	406·4	406·7	138·6	138·65	138·6
100	368·5	369·2	411·0	411·6	141·6	141·4	141·6
250	372·3	373·6	415·3	416·4	145·2	—	144·75
500	374·9	375·0	418·0	418·6	146·7	146·5	146·55
1000	375·8	375·9	419·5	419·0	147·7	—	147·75
2500	377·2	—	420·7	—	149·1	—	149·22
∞	(378·2)	—	(422·0)	—	(150·1)	(150·6)	—

even the slightest trace of water, this solvent has not been studied in this investigation. Results can be extrapolated for pure acetone from the values given, but it is hoped in the future to investigate the problem experimentally, as the only data available are very incomplete (Carrara, *Gazzetta*, 1897, **27**, i, 207; Sackur, *Ber.*, 1902, **35**, 1248).

The values for hydrogen chloride are all observed values, being uncorrected, and those for potassium chloride corrected by subtraction of the solvent conductivity. Kendall (*J. Amer. Chem. Soc.*, 1917, **39**, 7) gives 379·1 as the most probable value of λ_∞ for hydrogen chloride in water at 18°, and 422·7 at 25°.

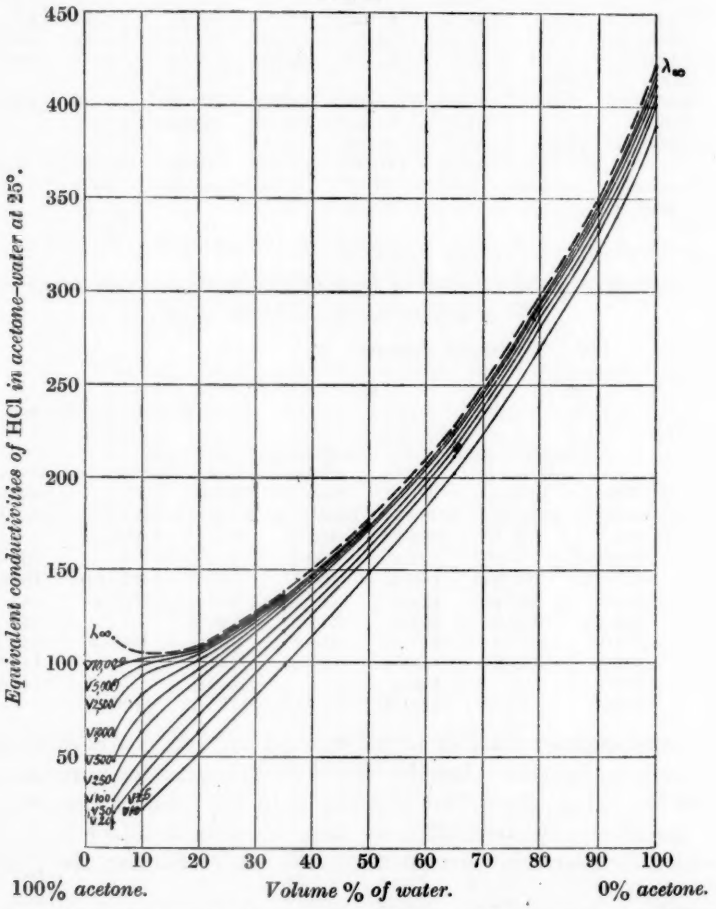
References.—Goodwin and Haskell, *Physical Rev.*, 1904, **19**, 380. Bray and Hunt, *J. Amer. Chem. Soc.*, 1911, **33**, 781. Melcher,

see Noyes and Falk, *ibid.*, 1912, **34**, 154. Lorenz, *Z. angew. Chem.*, 1921, **116**, 161.

Discussion.

The Influence of the Solvent on the Equivalent Conductivity of Potassium Chloride and Hydrogen Chloride.—The influence of the

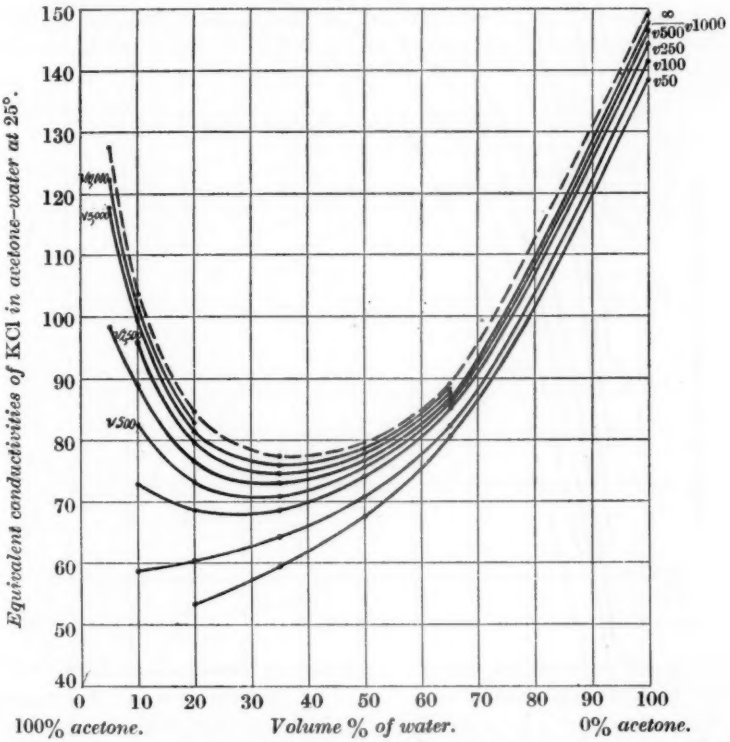
FIG. 1.



solvent upon the equivalent conductivity of hydrogen chloride in these acetone–water mixtures is extremely marked (Fig. 1). According to the classical theory of electrolytic dissociation, this arises from two causes; first, the effect of the solvent upon the migration velocities of the individual ions and secondly, upon the degree of dissociation of the electrolyte. The equivalent conductivity at infinite dilution falls rapidly as water is replaced by acetone up to

about 85% of acetone by volume, followed by an increase of conductivity in acetone–water mixtures richer in acetone. The effect of alteration in the degree of dissociation of the electrolyte is shown by the equivalent conductivities at finite dilutions and accounts for the points of inflexion in the equivalent conductivity–composition of the solvent curves (Fig. 1) at the acetone–water mixture containing 10% by volume of water, where the solvent has a marked effect upon the degree of dissociation of the electrolyte (Fig. 3).

FIG. 2.

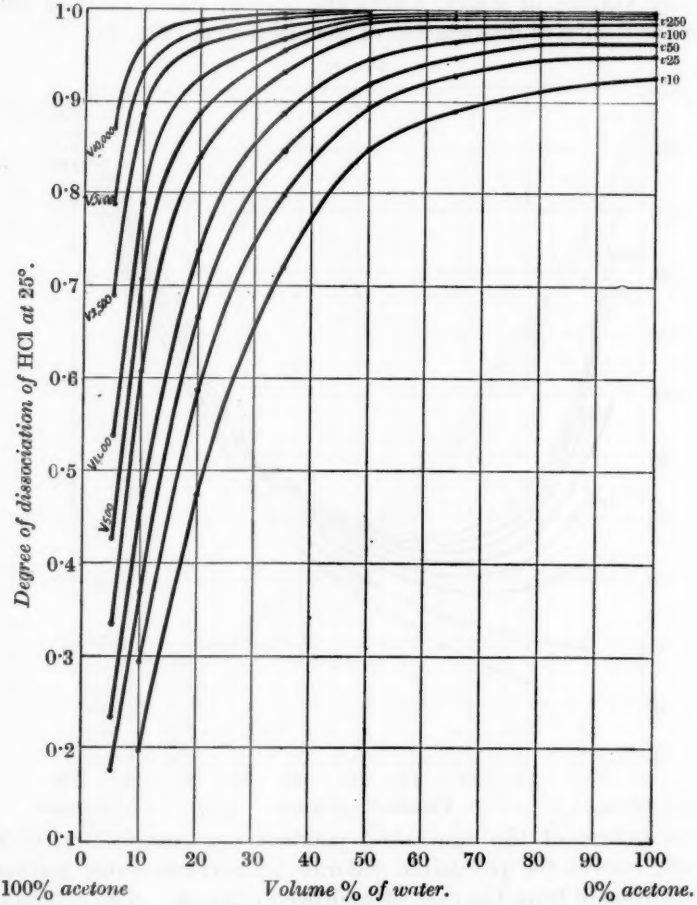


The nature of the equivalent conductivity–composition of the solvent curves for potassium chloride in acetone–water mixtures differs greatly from the case of hydrogen chloride. The equivalent conductivity at infinite dilution falls to a minimum in the solvent containing 40% by volume of water (Fig. 2), but owing to the effect of the fall in degree of the dissociation of this electrolyte with increase in acetone content of the solvent (Fig. 4), this minimum changes with dilution and indeed in the case of dilutions $v = 50$; $v = 100$, no minimum is observable within the limited range of acetone–water mixtures which can be studied at those concen-

trations on account of the low solubility of potassium chloride in mixtures rich in acetone.

Numerous investigators have attempted to show the dependence of the equivalent conductivity at infinite dilution on the physical properties of the solvent. Hartley, Thomas, and Applebey (J.,

FIG. 3.



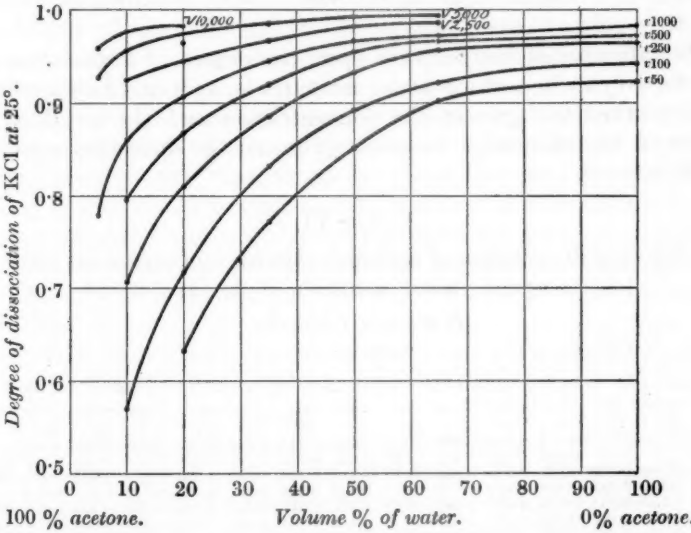
1908, **93**, 538), on the assumption of the applicability of Stokes' law to an ion moving with a spherical solvent atmosphere surrounding it, have shown that if the ionic radii of the anion and kation respectively do not vary with the composition of the solvent, then $\lambda_\infty \eta$ = constant, where η is the viscosity of the solvent.

Walden (*Z. physikal. Chem.*, 1906, **52**, 242; 1911, **78**, 273, 278, etc.) has shown that the product $\lambda_\infty \eta$ is constant and independent

of the temperature for tetramethylammonium iodide, tetrapropylammonium iodide, potassium iodide and other organic salts in a large number of organic solvents, but he has also shown that solvents with large association factors and high dielectric constants give variations from this rule. Creighton (*J. Franklin Inst.*, 1919, **187**, 33) found that deviations were shown by trimethyl-*p*-tolylammonium iodide in several organic solvents.

The viscosities of acetone–water mixtures rise to a maximum in the solvent containing approximately 60% by volume of water (Davis, Hughes, and Jones, *Z. physikal. Chem.*, 1913, **85**, 535), whereas the equivalent conductivity at infinite dilution of potassium

FIG. 4.



chloride in acetone–water mixtures has been shown in the present research to be a minimum in the solvent containing 40% of water by volume. No constancy of the expression $\lambda_\infty \eta$ can be expected. The equivalent conductivity of the electrolyte at infinite dilution is therefore dependent not only on the viscosity of the solvent but also on its other physical properties, for example, its state of association and dielectric constant.

In aqueous solutions the conductivity of hydrogen chloride is exceptional owing to the high value of the mobility of the hydrogen ion. In acetone–water mixtures of high acetone content, however, the mobility of the hydrogen ion does not differ greatly from that of the potassium ion, as the equivalent conductivity of hydrogen chloride at infinite dilution is only slightly higher than that of

potassium chloride in the acetone–water mixture containing 10% by volume of water. In the solvent containing 5% by volume of water, it is actually smaller.

The Influence of the Solvent on the Degree of Dissociation.—The influence of the solvent upon the degree of dissociation of electrolytes has been formulated in the well-known Nernst–Thomson rule.

Bruhl (*Z. physikal. Chem.*, 1899, **30**, 1) has pointed out that no absolute proportionality can exist between the dissociating power and the dielectric constant of the solvent, as the latter varies greatly with temperature and also with frequency.

The values of the degree of dissociation of hydrogen chloride and potassium chloride calculated from the expression $\alpha = \lambda_v/\lambda_\infty$ are in Table VI, and the influence of the solvent is shown in Figs. 3 and 4.

The influence of temperature upon the degree of dissociation of the electrolytes in acetone–water mixtures is, as would be expected, more marked the greater the concentration and the smaller the degree of dissociation of the electrolyte and the dielectric constant of the solvent.

TABLE VI.

The degree of dissociation of hydrogen chloride and potassium chloride in acetone–water mixtures at 20° and 25°.

Hydrogen Chloride.

	Volume % of water													
	5		10		20		35		50		80		100	
v	20°	25°	20°	25°	20°	25°	20°	25°	20°	25°	20°	25°.	20°.	25°
10	—	—	0·201	0·198	0·480	0·472	0·725	0·718	0·852	0·847	0·908	0·906	0·928	0·925
25	—	—	0·295	0·292	0·592	0·586	0·802	0·795	0·899	0·894	0·947	0·945	0·953	0·950
50	0·178	0·176	0·373	0·369	0·674	0·668	0·850	0·844	0·923	0·920	0·965	0·963	0·965	0·963
100	0·236	0·233	0·463	0·459	0·744	0·738	0·892	0·885	0·949	0·946	0·975	0·974	0·974	0·974
250	0·337	0·334	0·605	0·601	0·843	0·838	0·937	0·931	0·977	0·975	0·984	0·984	0·984	0·984
500	0·431	0·428	0·704	0·701	0·889	0·885	0·958	0·954	0·986	0·985	0·991	0·990	0·991	0·991
1,000	0·541	0·538	0·789	0·788	0·926	0·924	0·969	0·966	0·993	0·992	0·994	0·995	0·994	0·994
2,500	0·691	0·690	0·883	0·883	0·964	0·962	0·982	0·980	0·996	0·995	0·997	0·998	0·997	0·997
5,000	0·787	0·788	0·931	0·931	0·975	0·975	0·989	0·989	0·998	0·997	—	—	—	—
10,000	0·870	0·870	0·963	0·962	0·987	0·987	0·994	0·994	0·999	0·998	—	—	—	—

Potassium Chloride.

	Volume % of water.													
	5		10		20		35		50		65		100	
v	20°	25°	20°	25°	20°	25°	20°	25°	20°	25°	20°	25°	20°	25°
50	—	—	—	—	0·635	0·630	0·781	0·773	0·853	0·850	0·907	0·902	0·928	0·923
100	—	—	0·575	0·568	0·718	0·714	0·839	0·834	0·896	0·892	0·926	0·921	0·948	0·943
250	—	—	0·712	0·704	0·814	0·811	0·891	0·886	0·936	0·932	0·958	0·956	0·969	0·967
500	—	—	0·798	0·796	0·869	0·866	0·923	0·918	0·954	0·954	0·968	0·965	0·977	0·977
1,000	0·775	0·770	0·860	0·858	0·909	0·906	0·949	0·944	0·967	0·965	0·976	0·973	0·983	0·983
2,500	—	—	0·924	0·924	0·946	0·944	0·967	0·966	0·982	0·982	0·986	0·985	0·994	0·993
5,000	0·925	0·923	0·958	0·956	0·962	0·962	0·983	0·982	0·991	0·990	0·992	0·992	—	—
10,000	0·960	0·958	0·978	0·977	0·979	0·980	—	—	—	—	—	—	—	—

The values of the Ostwald expression, $\alpha^2/(1 - \alpha)v$, show considerable alteration with dilution in water or acetone–water solvents and

in no case is a true constant obtained, but in mixtures rich in acetone the change with dilution is much less marked.

Summary.

(1) The electrical conductivities of hydrogen chloride and potassium chloride have been measured over a wide range of dilution at 20° and 25° in acetone–water mixtures containing from 5 to 100% of water by volume.

The equivalent conductivity of hydrogen chloride at infinite dilution falls sharply to a minimum in the solvent containing about 85% of acetone, after which the change is small, an increase being noticed in solvents very rich in acetone. In other solutions, the equivalent conductivity falls as the acetone content increases, as the result of the influence of the solvent upon the degree of dissociation of the electrolyte as well as upon the migration velocities of the individual ions.

The equivalent conductivity of potassium chloride at infinite dilution falls to a well-defined minimum in the solvent containing approximately 40% by volume of water, but at other dilutions, owing to the change in degree of dissociation of the electrolyte, this minimum shifts and in more concentrated solutions, $v = 100$ and $v = 50$, no minimum is observable in any acetone–water mixture in which the solubility of this electrolyte allows the measurement to be made.

(2) It is shown that the use of platinised platinum electrodes is not attended by error due to catalytic influence upon the acetone in the mixed solvents studied.

(3) The influence of temperature upon the degree of dissociation of these electrolytes is more marked the higher the acetone content of the solvent and the higher the concentration of the solution.

(4) The Ostwald dilution law does not hold fully in any acetone–water mixture investigated, but, as the acetone content increases, gives values more nearly approaching a constant at all dilutions.

We wish to express our indebtedness to Dr. G. Rotter, C.B.E., and Dr. J. N. Pring for their interest in this work, which is published by permission of the Director of Artillery, War Office.

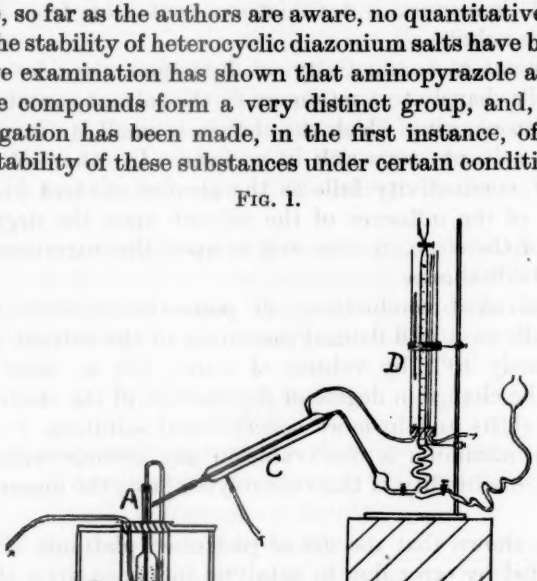
RESEARCH DEPARTMENT,
ROYAL ARSENAL, WOOLWICH. [*Received, August 21st,* 1925.]

CCCCVI.—*The Velocity of Decomposition of Heterocyclic Diazonium Salts. Part I. Diazonium Salts of the Pyrazole and Pyrazolone Series.*

By JOSEPH REILLY and DENIS MADDEN.

HITHERTO, so far as the authors are aware, no quantitative measurements of the stability of heterocyclic diazonium salts have been made. Qualitative examination has shown that aminopyrazole and aminopyrazolone compounds form a very distinct group, and, therefore, an investigation has been made, in the first instance, of the comparative stability of these substances under certain conditions. The

FIG. 1.



physicochemical method of Hausser and Müller (*Bull. Soc. chim.*, 1892, **7**, 721), or the modification of it devised by Cain and Nicoll (J., 1902, **81**, 1412), was found unsuitable for this particular problem, owing to the extraordinary comparative stability of some of the compounds examined, and the consequent exceptionally long period of time during which the reaction had to be followed. The process adopted by the authors was to heat a definite volume of a solution containing a known weight of the amine (sufficient to give 56 c.c. of gas at *S.T.P.*, normal diazotisation being assumed) in a specially constructed quartz vessel, A (Fig. 1), fitted with a ground stopper into which was sealed a tube passing to the bottom of the vessel. The vessel was contained in a thermostat, B, at 101·5°, which temperature was found to keep the solution of the diazonium salt at 100°, and was connected through a condenser, C, to a water-jacketed nitrometer, D. A current of air-free carbon dioxide was

periodically passed through the solution, and the liberated nitrogen was collected over concentrated aqueous potassium hydroxide.

By this method it is possible to overcome the difficulties met with by earlier investigators. The air is completely expelled from the apparatus, the vessel containing the solution is placed in the thermostat, and a current of carbon dioxide is passed through it until the temperature becomes constant (the necessary time having been determined in a control experiment); the nitrogen evolved during this time is collected and measured. It is thus possible to have an exact starting point for a solution of definite concentration. Further, no allowances such as had to be made by former investigators are necessary for the expansion of the solution and of the air in the apparatus. (The apparatus is so arranged that the air space between the surface of the solution and the mercury in the nitrometer is as small as conveniently possible.)

1-*Phenyl*-2 : 3-*dimethylpyrazolone*-4-*diazonium Chloride* (*Antipyrine*-4-*diazonium Chloride*).—A solution of 0·5075 g. of 4-aminoantipyrine in air-free water and 7·5 c.c. of *N*-hydrochloric acid (3 equivs.) was treated with 20 c.c. of aqueous sodium nitrite (1·73 g. per 200 c.c.), and the resulting solution made up to 70 c.c. The solution of the diazonium salt, originally pale yellow, developed a reddish-brown colour on warming. This evidence of a secondary reaction is supported by the fact that after 90% of the substance had decomposed the rate of gas evolution declined rapidly. The decomposition, however, was mainly a unimolecular reaction. In the table, x = the volume of nitrogen evolved after t hours (measured at 22° and 766 mm.), and $k = 1/t.\log\{a/(a-x)\}$, where a = the theoretical volume of " diazo "-nitrogen under the same conditions (= 60 c.c.).

t.	x.	$k \times 10^3$.	t.	x.	$k \times 10^3$.	t.	x.	$k \times 10^3$.
0	0·2	—	7	34·4	52·84	14½	49·6	52·50
1	8·0	62·15	8	37·5	53·20	15½	50·5	51·60
2	13·4	54·80	9	40·1	53·20	16½	51·2	50·60
3	18·2	52·32	10	42·4	53·31	17½	51·8	50·00
4	22·7	51·61	11	44·3	53·00	20½	53·0	46·00
5	27·0	51·93	12	46·1	52·93	22½	53·4	—
6	30·8	52·13	13	47·7	53·00			

Neither the addition of excess of acid nor the introduction of a small amount of colloidal gold had any marked effect on the rate of decomposition.

Antipyrine-4-*diazonium Nitrate*.—The rate of decomposition was of the same order as that of the chloride. The amount of secondary reaction was, however, slightly greater, the rate of gas evolution falling off more rapidly towards the end.

Antipyrine-4-*diazonium Sulphate*.—The rate of decomposition was

much more rapid at the beginning, and did not follow the unimolecular law, the value of k falling from 0·1305 (8 c.c. in the first ½ hour) to 0·0544 (38·8 c.c. in 9 hours); a being 57·35 c.c. That the amount of secondary reaction was considerably greater was shown by the more marked deepening of colour, and the formation of a dark reddish-brown precipitate.

The rate of decomposition, then, is in this case, considerably influenced by the nature of the anion, unlike the results obtained by Cain (*Ber.*, 1905, **38**, 2511) with benzenoid diazonium salts.

3 : 5-*Dimethylpyrazole*-4-*diazonium Chloride*.—4-Amino-3 : 5-dimethylpyrazole (0·2775 g.) was dissolved in 15 c.c. of *N*-hydrochloric acid (6 equivs.) and treated as in the foregoing cases. The amount of decomposition in 3 hours was almost inappreciable, less than 2% of the total "diazo"-nitrogen being evolved. In a second experiment, 3 equivs. of acid being used, the decomposition followed the peculiar course indicated by the following figures:

Pressure = 756 mm. Temp. = 18°. a = 60 c.c.

t	0	1	2	3	4	5	6	7
x	0·0	1·0	2·4	4·2	6·0	7·8	9·7	11·6
t	8	9	10	11	12	14	16	18
x	13·5	15·4	17·4	19·4	21·4	25·0	28·7	32·1
t	20	24	28	32	36	40	44	48
x	35·0	40·6	45·4	49·3	52·1	54·6	56·2	57·2

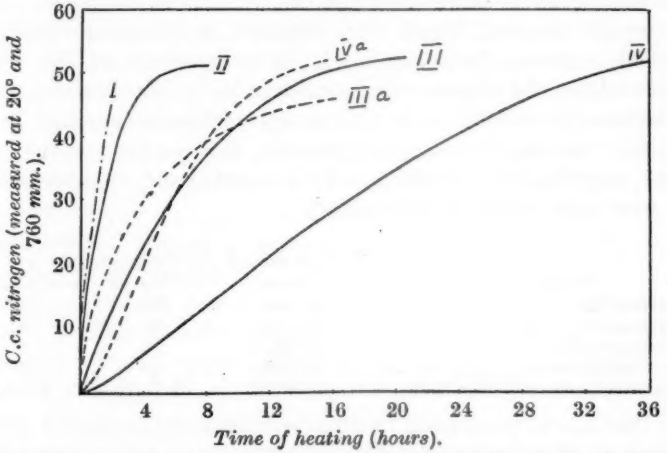
These figures show that even after 48 hours' heating the decomposition of the diazonium salt is not complete. It is evidently irregular at the beginning, less nitrogen being evolved during the first hour than during any of the subsequent 20 hours. This behaviour is probably due to the existence of two isomeric forms of the diazonium chloride, and this view is supported by the fact that when a small quantity of the base is diazotised at the ordinary temperature and added to alkaline β-naphthol, no coupling takes place for some time, whereas a colour is immediately developed if the diazonium solution has previously been boiled for a few minutes. After the fourth hour, the decomposition proceeds with some degree of regularity, but not in accordance with the unimolecular law.

3 : 5-*Dimethylpyrazole*-4-*diazonium Sulphate*.—As in the case of the chloride, the reaction was irregular at the beginning. From the end of the fourth hour to the end of the twelfth hour the rate of decomposition followed the unimolecular law, the mean value of k being 0·0720. A solution of the diazonium salt containing an excess of sulphuric acid (6 equivs.) was remarkably stable, only 2% of the total "diazo"-nitrogen being evolved in 3 hours.

Pyrazole-4-*diazonium Chloride*.—3 : 5-Dimethylpyrazole was converted by Knorr's method (*Annalen*, 1894, **279**, 218) into the corre-

sponding 3 : 5-dicarboxylic acid, the latter, however, being isolated from the oxidation product by the addition of hydrochloric acid without the intermediate formation of the acid potassium salt. Pyrazole, obtained by heating the dry dicarboxylic acid at 270—275°, was converted by Buchner and Fritsch's method (*Annalen*, 1893, **273**, 265) into the 4-nitro-compound. This was isolated by adding ice to the nitration mixture, and was reduced as follows: A solution of 3 g. of the nitropyrazole in 100 c.c. of moist ether was treated, with cooling, with a large excess of an aluminium–mercury couple during a few hours, complete reduction being indicated by

FIG. 2.



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the disappearance of the purple colour initially developed. The ether was distilled off, the residue extracted a few times with boiling alcohol, air being excluded, and the extract was immediately treated with hydrochloric acid. The product was evaporated, and the residue recrystallised from alcohol; 4-aminopyrazole dihydrochloride then separated. As the quantity obtained was small, the somewhat dark product was not further purified before diazotisation.

The rate of decomposition of the diazonium chloride from 0·39 g. of the dihydrochloride approximately obeyed the unimolecular law. In 5 hours, 83% of the total "diazo"-nitrogen was evolved, but thereafter the rate of decomposition declined very rapidly. The much more rapid decomposition of this substance seems to indicate

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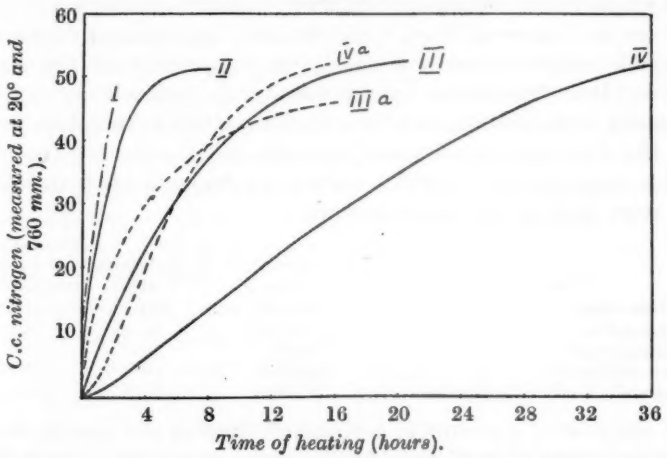

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The rate of decomposition of the diazonium chloride from 0·39 g. of the dihydrochloride approximately obeyed the unimolecular law. In 5 hours, 83% of the total "diazo"-nitrogen was evolved, but thereafter the rate of decomposition declined very rapidly. The much more rapid decomposition of this substance seems to indicate

that the methyl groups in diazotised 3 : 5-dimethylaminopyrazole have a stabilising influence on that diazonium salt.

The comparative stability of the diazonium chlorides from 4-aminoantipyrine, 4-amino-3 : 5-dimethylpyrazole, and 4-aminopyrazole may be judged from the curves in Fig. 2, showing the rate of gas evolution at various intervals.

Of the large number of benzenoid diazonium salts investigated by Cain and Nicoll (*loc. cit.*) the most stable (and the only two apparently sufficiently stable for examination at 100°) were those from *o*- and *m*-nitroaniline. The conditions under which the experiments described above were carried out were different from those employed by earlier investigators, but results closely analogous to those of Cain and Nicoll were obtained in a control experiment in which *o*-nitroaniline was used. A comparison of the results obtained from the diazonium chlorides in the pyrazole and pyrazolone series with those from *o*- and *m*-nitroaniline is therefore justifiable (for 4-amino-3 : 5-dimethylpyrazole, the results are the mean of the experiments in which only 3 equivalents of hydrochloric acid were used in the diazotisation).

Substance.	k (t measured in mins.).	% Decomp. in first hr.	Time (mins.) for half decomposition.
m-Nitroaniline	0·0332	100	10
o-Nitroaniline	0·00564	54	53
4-Aminopyrazole	0·00317	40	80
4-Aminoantipyrine	0·00088	13	360
4-Amino-3 : 5-dimethylpyrazole	0·00030	1·7—2	1020

In the case of 4-amino-3 : 5-dimethylpyrazole the rate of decomposition of the diazonium chloride was considerably slower (3 to 4 times) when excess of acid (6 equivs.) was employed. It cannot be said, as of benzenoid salts, that the rate of decomposition in the case of heterocyclic diazonium salts is uninfluenced by the nature of the anion, for the diazonium sulphates of both 4-aminoantipyrine and 4-amino-3 : 5-dimethylpyrazole decomposed much more rapidly than the corresponding chlorides.

UNIVERSITY COLLEGE, CORK. [*Received, September 7th*, 1925.]

CCCCVII.—*The Swelling and Dispersion of Some Colloidal Substances in Ether–Alcohol Mixtures.*

By ERNEST WALTER JOHN MARDLES.

IT is well known that cellulose nitrate and Kauri copal each dissolve readily in a mixture of ethyl alcohol and ethyl ether, although the liquids taken singly are non-solvents, and that the solubility of

potassium stearate, sandarac resin, or night-blue in such a mixture is greater than the mean value of the solubilities in either constituent. This characteristic solvent action appears to be general with a large number of colloidal substances and mixtures of liquids, *e.g.*, gelatin in water–acetic acid, potassium oleate in alcohol–water, casein in pyridine–water, but no satisfactory explanation of it appears yet to have been made. Baker's view that in ether–alcohol mixtures the intrinsic solvent for cellulose nitrate is a loose molecular complex of alcohol and ether (J., 1912, **101**, 1409) has been considerably criticised (Report of Discussion on Colloids held jointly by the Faraday and Physical Societies, 1920). Barr and Bircumshaw have proposed the hypothesis, previously rejected by Baker, that the " best solvent " of cellulose nitrate is unimolecular alcohol.

A close study of the phenomena, in particular the gelation of the sols and swelling behaviour, indicates that a complete explanation must involve the significant fact that swelling precedes dispersion. The important bearing that swelling has on peptisation or dispersion in mixed liquids was recognised many years ago by Tompkins (*op. cit.*, appendix 2), but his view that dispersion is an extreme case of what in lesser degree is known as swelling is now regarded as erroneous.

It appears that the ether in an ether–alcohol mixture not only acts as a diluent, disturbing the equilibrium $(R{\cdot}OH)_n \rightleftharpoons nR{\cdot}OH$, but also actually enters the complex which the molecules of the dispersion medium form with the colloid.* Baker pointed out that when the ether is replaced by another non-solvent there is not necessarily formed a solvent mixture for cellulose nitrate. Although he was probably right in ascribing to the ether an active part in the solvent action, yet his hypothesis as to the particular mode of action is not in accord with fact.

It has been found as a general principle that the characteristic solvent action of mixed liquids cannot be ascribed to the intrinsic action of one kind of molecule or molecular complex, but whenever molecular simplification occurs in a liquid mixture there is increased solvent action. Therefore, when compound formation occurs between the components of a binary mixture, loss of solvent power is to be expected. Indeed, it is possible to use a colloidal substance, *e.g.*, cellulose acetate, to detect the presence of a molecular compound in a system of liquids (Mardles, J., 1924, **125**, 2244).

The action of mixed liquids on colloids presents a number of striking features both with regard to swelling and to peptisation. If cellulose nitrate be soaked in dry ether or absolute alcohol, there

* Kugelmass (*Rec. trav. chim.*, 1922, **41**, 751) has shown that ether favours the peptisation of cellulose dinitrate, and alcohol that of the trinitrate.

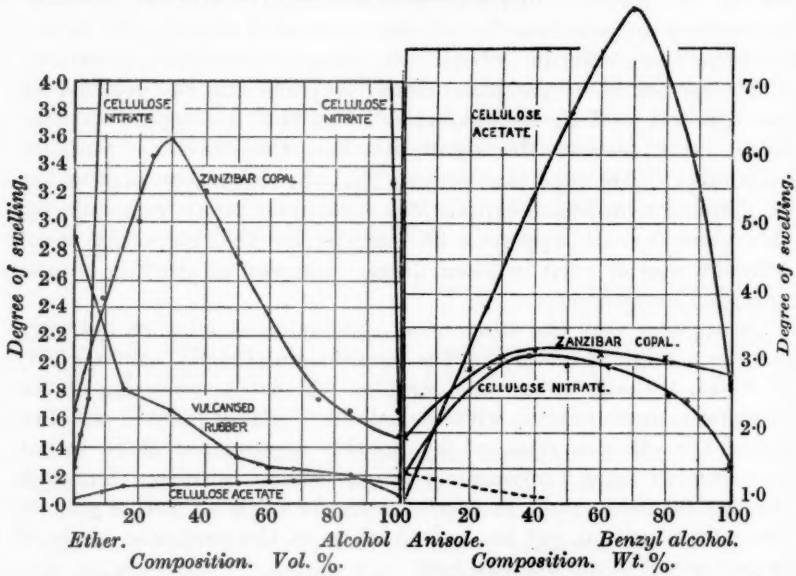
is little apparent change even if the temperature be varied from − 80° to + 100°, but a certain amount of swelling occurs. With the addition of the second liquid there is a rapid increase in the degree of swelling. For example, a film of cellulose nitrate, after immersion at the ordinary temperature for a few days, increased 28% in weight in dry ether and 68% in absolute alcohol; in ether containing 5% (vol.) of alcohol the increase was 75%, and any

FIG. 1.

The swelling of some colloidal substances in mixtures of ethyl alcohol and ethyl ether at 18° after 7 days' immersion.

FIG. 3.

The swelling of some colloidal substances in mixtures of anisole and benzyl alcohol.



About 10–15% of the copal dissolved. The values for this substance refer to the undissolved portion and were obtained by determining the amount of resin in the swollen clot.

The chained line indicates the swelling of cellulose nitrate in a mixture of anisole and phenol.

further addition of alcohol resulted in a very high degree of swelling. Similarly, the addition of 2·5% of ether to alcohol increased the swelling to such an extent that less than one-third of the swollen mass was cellulose nitrate and dispersion of the more soluble constituents began.*

In Fig. 1 are shown the degrees of swelling, in ether–alcohol mixtures, of (*a*) cellulose nitrate, (*b*) Zanzibar copal, (*c*) vulcanised

* The cellulose esters, like cellulose, and other colloidal substances, *e.g.*, the resins, are heterogeneous and it is possible to separate them into fractions of different solubility and viscosity.

rubber, and (*d*) cellulose acetate. The degree of swelling is expressed as the weight of the swollen mass obtained from 1 gram of the dry colloid.

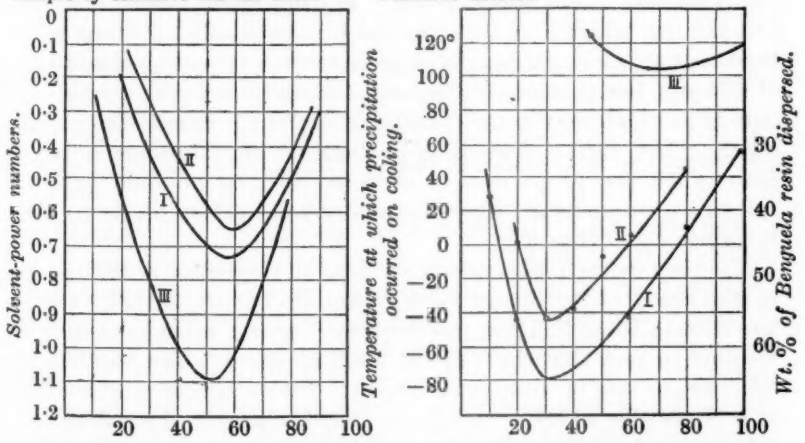
Materials.—The ether was dried over sodium and fractionated. Absolute alcohol was used. The cellulose nitrate (N, 10·7%) was obtained in film form by leaving an acetone solution to evaporate slowly in a flat dish. The film was thoroughly dried by leaving it in the air for several months. About 0·5 g. of the film was

FIG. 2.

The solvent power of ethyl alcohol–ethyl ether mixtures for cellulose nitrate, Kauri gum, etc.

Cellulose nitrate. I, *Nitrogen content*, 10·7%. II, *Nitrogen content*, 11·5%. III, *Approximately 5% of water present in the solvent mixtures, and another sample of cellulose nitrate used.*

I, *Kauri copal.* II, *Benguela copal.* III, *Cellulose acetate.*



The solvent-power numbers were obtained by noting the relative quantities of a diluent, e.g., hexane, required to be added to 1 c.c. of the sol (concentration 5/100; temperature 20°) in order to start precipitation of the colloid.

immersed in about 20 c.c. of the liquid. The Zanzibar copal used was from the same sample throughout, and the vulcanised rubber consisted of ordinary black rubber tubing extracted with acetone. The cellulose acetate (Rhône) had an acetyl content of 39·6%, corresponding with the formula $C_{12}H_{15}O_5(O{\cdot}CO{\cdot}CH_3)_5$.

The swelling results obtained for cellulose nitrate when dispersion did not occur seem to indicate that the degree of swelling in ether–alcohol mixtures tends to increase enormously with further additions of the second liquid. The experiments of Masson, who found that fibrous cellulose nitrate absorbed a maximum amount of

ether–alcohol vapour when this was composed of 1 mol. of ether and 1 mol. of alcohol, apparently support this view (*op. cit.*, p. 95).

It is significant that the optimum solvent mixture of alcohol and ether for cellulose nitrate has an equimolecular composition only when a little water is present. It contains more alcohol if the materials have been carefully dried (compare Stepanow, *Z. ges. Schiess-u. Sprengstoffw.*, 1907, **2**, 43; Matteoschat, *ibid.*, 1914, **9**, 105).

The close relationship between the degree of swelling and solvent action is shown clearly in the case of the copal resins. Zanzibar copal, one of the harder and more intractable copals, swells considerably in ether–alcohol mixtures, but the amount of dispersion is small. On the other hand, the softer Kauri resin dissolves in the mixtures and, on cooling sufficiently, either the solution gelates or the resin is precipitated as an amorphous mass. With Benguela copal of intermediate hardness, a part of the resin is dispersed and the remainder swells considerably. The optimum solvent mixture, *i.e.*, the one which dissolves the resins most readily, forming solutions that are most stable against precipitation by cooling or addition of diluents, has practically the same composition as the mixture of liquids in which maximum swelling occurs in the case of the harder copals. The degree of swelling of Zanzibar copal reaches a maximum when the proportion of ether is 70% by volume (Fig. 1), and this mixture exerts the maximum solvent action on Kauri and Benguela copal (Fig. 2).

The very marked influence of swelling on dispersion is also shown by the study of the binary mixture anisole–benzyl alcohol. Cellulose nitrate is swollen but not dispersed by this mixture, and it is possible to plot the whole of the swelling curve. The swelling of cellulose acetate is considerable and dispersion occurs on warming, so it is possible to note the relation between degree of swelling and solvent action. Towards the copals, this binary mixture behaves as the previous one (Table I and Fig. 3).

The anisole used had d_4^{25} 0·989 and b. p. 155°. Of the benzyl alcohol, $d^{25°}$ 1·043, 95% distilled between 205° and 206°.

It is seen from Table I that the swelling of cellulose nitrate continues in anisole during the 31 days, but becomes constant in some of the mixtures after 15 days. This fact, that the rate of swelling is highest when the swelling is greatest, is of importance in explaining why the " best " solvent mixture disperses the most rapidly; for not only does the optimum solvent mixture often form the least viscous sol, so that the resistance to the diffusion of the colloidal particles from the surface during dispersion is at a minimum, but also the initial swelling of the colloid is most rapid.

Table I.

The swelling action of mixtures of benzyl alcohol and anisole at 18°. *a* denotes the wt.% of anisole in the mixture, and *b* the degree of swelling.

Cellulose nitrate.

a	100	74	62·2	50	37·5	28	19·2
b after 7 days	1·25	1·75	3·06	2·0	2·12	2·13	—
„ 15 „	1·35	2·80	3·22	2·90	2·98	2·83	1·5
„ 21 „	1·42	2·87	3·22	2·90	2·98	2·85	2·1
„ 31 „	1·47	2·92	3·22	2·90	2·98	—	2·55
a	13·7	9·6	0				
b after 7 days	1·37	—	1·11				
„ 15 „	1·80	1·85	1·27				
„ 21 „	2·25	2·2	1·4				
„ 31 „	2·5	2·4	1·56				

Zanzibar copal.

a	100	80	70	60	40	20	0
b after 2 days	1·45	2·1	1·9	2·2	2·0	2·2	2·1
„ 5 „	1·93	2·9	3·1	3·2	3·1	3·1	2·8
„ 27 „ *.....	2·0	4·1	4·2				

(i) *Cellulose acetate* and (ii) *Gelatin* (Coignet's).

a	100	75	47·5	30	12	0
b after 5 days (i) ...	1·09	3·85	6·6	8·2	6·0	2·6
„ „ (ii) ...	1·06	1·05	1·00	1·00	1·03	1·07

* By this time the resin was very soft and tacky and very difficult to manipulate.

The swelling of cellulose acetate is at the maximum in the benzyl alcohol–anisole mixture containing 50% of anisole, and Table II shows that this is also the optimum solvent mixture. Similarly, the composition of the best solvent mixture for Kauri copal is practically that of the mixture in which Zanzibar copal swells the most. Air-dried cellulose acetate dissolved in benzyl alcohol on warming. On cooling rapidly, a 5% sol became turbid at 18° owing to separation of the acetate. The temperature of separation was first lowered and then raised on addition of anisole.

Table II.

The solvent action of mixtures of benzyl alcohol and anisole on cellulose acetate and Kauri copal.

w = wt.% of anisole and t = temperature of precipitation or gelation.

Cellulose acetate.

w	0	12	26	40	54	66	72	78
t	18°	10°	5°	4°	12°	38°	65°	90°

Kauri copal.

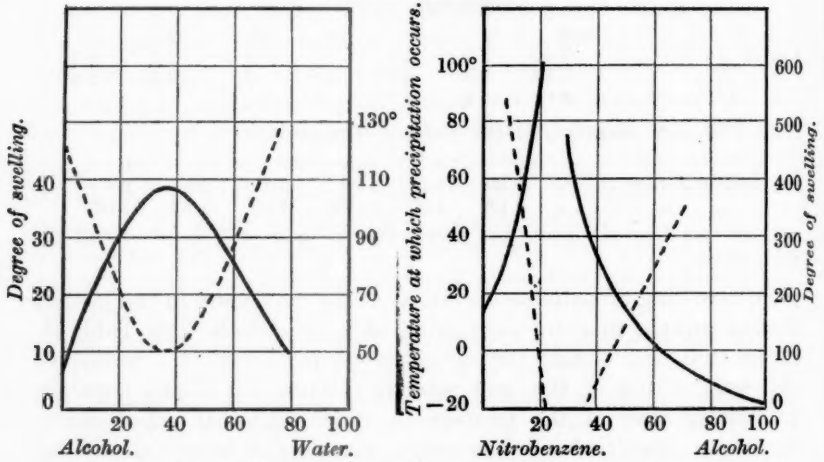
w	100	90	75	60	40	20	0
t	90°	33°	−25°	−60°	−52°	−42°	−22°

The Kauri copal dissolved in anisole on warming, but separated when the temperature fell below 90°. The addition of benzyl alcohol facilitated the dispersing action and the solutions were stable at lower temperatures.

The important influence of swelling on dispersion can be shown equally well with other binary mixtures, *e.g.*, alcohol and water. Knoevenagel and his co-workers (*Koll. Chem. Beiheft*, 1921, 1922, 1923) have measured the swelling of cellulose acetate in a number of binary mixtures, and the solvent action of many of these mixtures on the same substance has been determined (Mardles, *J. Soc.*

FIG. 4.

The correlation of the swelling of cellulose acetate in binary mixtures (Knoevenagel) with solvent action.



—— *Degree of swelling (Knoevenagel)*; --- *Temperature of precipitation (Mardles*, loc. cit.).

Chem. Ind., 1923, **42**, 127). There is a close correlation in most cases, although different varieties of cellulose acetate were used.

Gelatin and vulcanised rubber differ from the cellulose esters and the resins in that their degree of swelling in ether–alcohol mixtures is less than the mean value.

The swelling of cellulose nitrate in phenol–anisole is quite different from that in benzyl alcohol–anisole, there being no maximum to the curve.

TABLE III.

The swelling of cellulose nitrate in phenol–anisole mixtures.

Wt. % of phenol	0	10	27·5	44
Degree of swelling	1·47	1·39	1·21	1·07

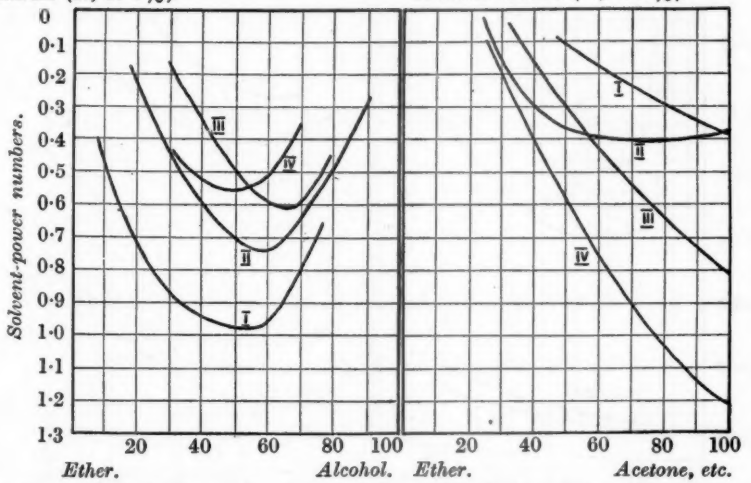
A parallel behaviour is found in the dispersion process, for, if either ether or alcohol be replaced by another liquid, the characteristic solvent action of the ether–alcohol mixture is not necessarily repeated. The solvent power of various binary mixtures containing ether for the sample of cellulose nitrate used is shown in Fig. 5. The solvent power numbers were obtained in the manner already described (J., 1924, **125**, 2244).

The explanation of the characteristic dispersing action of mixed liquids must be sought in the cause of the increased swelling, and,

FIG. 5.

The solvent action of various binary mixtures of ethers and alcohols on cellulose nitrate (N, 10·7%).

The solvent action of various binary mixtures containing ethyl ether on cellulose nitrate (N, 10·7%).



I, *Benzyl methyl ether and ethyl alcohol.* II, *Ethyl ether and ethyl alcohol.* III, *Ethyl ether and benzyl alcohol.* IV, *Anisole and ethyl alcohol.*

I, *Ethyl ether and epichlorohydrin.* II, *Ethyl ether and acetic acid.* III, *Ethyl ether and acetone.* IV, *Ethyl ether and ethyl acetate.*

from the cases examined, the specific characters of the liquids and colloidal substances are evidently of primary importance. Cellulose nitrate in an ether–alcohol mixture probably attaches to its particles both kinds of molecules from the dispersion medium, and these attracted molecules may bind additional ones.

Esselen (*J. Ind. Eng. Chem.*, 1920, **12**, 801), discussing the characteristic solvent action of mixtures of chloroform and alcohol on cellulose acetate, puts forward a possible explanation based on the fact that cellulose and its compounds have marked affinities for the hydroxyl group of alcohol. Mixtures of liquids containing as one constituent a substance with reactive groups, such as an alcohol, ketone, or acid, especially if this constituent is the first

member of a homologous series, usually have markedly high solvent action. A liquid, such as hexane or xylene, which is not particularly reactive and is a high member of a homologous series behaves like a diluent or inert component in a binary mixture.

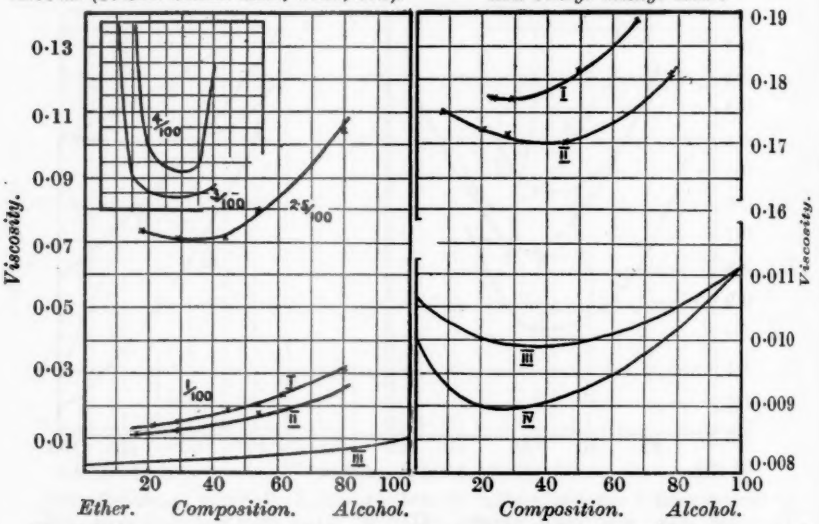
The structure of the complex formed by the molecules of the dispersion medium and a colloidal particle is apparently simple, for the composition of the best solvent mixture is often simple, molecularly (Mardles, J., 1924, **125**, 2244), and Knoevenagel has

FIG. 6.

The viscosity of solutions of cellulose nitrate in ether–alcohol mixtures.

Mixtures of ethyl alcohol and ethyl ether.
Inset: Viscosity results of Gibson and McCall (J. Soc. Chem. Ind., 1920, 172).

Mixtures of ethyl alcohol with anisole and benzyl methyl ether.



I, *Cellulose nitrate*, 11·5% N. II, *Cellulose nitrate*, 10·7% N. III, *Pure liquids.*

I, 2·5/100 *in anisole–ethyl alcohol.* II, 2·5/100 *in benzyl methyl ether–ethyl alcohol.* III, *Benzyl methyl ether–ethyl alcohol.* IV, *Anisole–ethyl alcohol.*

shown, in the case of the swelling of cellulose acetate in mixed liquids, that the proportion of the constituents in the swollen mass is often a simple molecular one also.

Viscosity and Density of the Sols.—The effect of the addition of a colloidal substance on the viscosity of a binary mixture of liquids is, in general, such that the shape of the viscosity–composition curve becomes exaggerated and any special feature of it is developed (Mardles, J., 1924, **125**, 2244). These effects are produced when cellulose nitrate is added to ether–alcohol mixtures (Table IV and Fig. 6). The sag in the viscosity curve for the pure liquids is exaggerated and, for the sols of higher concentration, there is a minimum

point, which occurs at a composition near that of the optimum solvent mixture.

TABLE IV.

The viscosity and density of sols of cellulose nitrate in mixtures of ethyl alcohol and ethyl ether.

Concentration of sol, 1/100. Nitrogen content of nitrate: a, 10·7%; b, 11·5%.

Wt. % of ether.	Difference in density between dispersion medium and sol.		Viscosity.	
	a.	b.	a.	b.
20·0	0·0045	0·0060	0·026	0·031
38·4	—	0·0074	—	0·024
47·2	0·0085	0·0077	0·019	0·021
56·7	—	0·0075	—	0·019
70·6	0·0078	0·0076	0·0136	0·015
78·0	—	0·0056	—	0·014
84·2	0·0065	0·0059	0·011	0·014

Concentration, 2·5/100. Nitrogen content, 10·7%.

20·0	0·0135	0·105
47·2	0·0174	0·080
56·7	0·016	0·072
71·6	0·013	0·072
84·2	0·014	0·074

TABLE V.

The viscosity and density of sols of cellulose nitrate in mixtures of benzyl methyl ether and ethyl alcohol.

Benzyl methyl ether, b. p. range 167—169°, $d^{25°}$ 0·963.

Wt. % of benzyl methyl ether.	Density.		Viscosity.	
	Liquids.	Sol, 2·5/100.	Liquids.	Sol, 2·5/100.
100	0·963	—	0·0107	—
92	0·9465	0·955	0·0104	0·175
78·9	0·932	0·9434	0·01001	0·1726
72·8	0·9189	0·9311	0·01007	0·172
55·3	0·8863	0·8983	0·01002	0·170
26·4	0·8322	—	0·01036	—
22	—	0·8455	—	0·181

The viscosity and density of sols of cellulose nitrate in mixtures of anisole and ethyl alcohol.

Wt. % of anisole.	Density difference.	Viscosity of sol, 2·5/100.
77·1	0·0113	0·1772
71·6	0·0116	0·177
51	0·0118	0·184
31·9	0·0115	0·189

From the differences in density between the dispersion medium and the sols it will be seen that the greatest volume changes occur when the compositions of the mixed liquids are near that corresponding to the maximum sag in the viscosity curve and when the solvent power of the mixed liquids is high (Fig. 5).

Surface-tension Measurements.—A large number of measurements of the surface tensions of the organosols in ether–alcohol mixtures and in the single liquids were made at different temperatures and for different concentrations by means of Sugden's maximum bubble pressure method (J., 1924, **125**, 27). In the case of ethyl alcohol and its mixtures with ethyl ether, benzyl methyl ether, and anisole, the effect of the addition of the colloidal substance was to *raise* the surface tension of the dispersion medium. Similarly, the ether organosols had higher surface tensions than the pure liquids.

The temperature coefficient of the surface tension from 10° to 30° for the organosols was practically the same as that for the pure dispersion medium.

Tables VI and VII give a selection of the results obtained.

TABLE VI.

Ethyl ether sols of concentration 1/100.	$\gamma^{25°}$ in dynes/cm.	Ethyl alcohol sols.	γ in dynes/cm.
(Ethyl ether).	16·6	(Ethyl alcohol).	21·7 at 28°
Chlorophyll.	16·65	Potassium oleate, 0·25/100.	22·1 „
Tung oil.	16·6	„ „ 0·5/100.	22·3 „
Copper oleate.	16·8	(Ethyl alcohol).	21·9 at 25°
Mastic (5/100).	16·85	Tannic acid, 2/100.	22·1 „
Dragon's blood.	16·8	„ „ 10/100.	22·7 „

The surface tension of ethyl alcohol was also raised slightly by the addition of shellac, night-blue, and potassium stearate, but no appreciable effect was produced by sandarac resin and chlorophyll.

TABLE VII.

The surface tension of some sols in ethyl ether–ethyl alcohol mixtures at 25°.

Wt. % of ether.	γ for the liquid.	Sols.	γ.
63·9	18·6	Cellulose nitrate, 5/100.	20·1
		„ „ 2/100.	19·7
		Chlorophyll.	18·8
		Dragon's blood, 2/100.	19·6
		Copper oleate, 2/100.	19·6
33·1	19·6	Cellulose nitrate, 5/100.	21·4
		„ „ 2/100.	20·1
		Chlorophyll, 2/100.	19·9
		Copper oleate, 2/100.	20·0
		Tannic acid, 2/100.	20·1
13·1	20·9	Chlorophyll, 2/100.	20·95
		Kauri resin, 5/100.	21·2

Chlorophyll had practically no effect on the surface tension of binary mixtures of alcohol with anisole or benzyl methyl ether, but cellulose nitrate raised it a little.

TABLE VIII.

Composition.	$\gamma^{25°}$ for the liquid.	Sols.	$\gamma^{25°}$.
Anisole, 71·6%.	27·7	Cellulose nitrate.	28·3
Benzyl methyl ether, 44%.	26·8	Night-blue.	27·2
		Cellulose nitrate.	28·3
" " 26·4%.	24·0	" "	25·2
		Dragon's blood.	24·5

The surface tension of a mixture of 2 vols. of benzyl alcohol and 1 vol. of anisole at 20° was raised from 37·3 to 38·2 by cellulose acetate (2/100), and slightly by night-blue.

Summary.

A study has been made of the swelling and the dispersion action of ether–alcohol mixtures on colloidal substances. The explanation of the high dispersing action of the mixed liquids must be sought in the cause of the colloidal substances swelling initially to a greater extent in the mixtures than in the liquids taken singly, there being a close correlation between the swelling and the dispersing action.

The attraction between a colloidal particle and the molecules of the mixed dispersion medium, due to the presence of mutually reactive groups, whereby complexes are formed, appears to reach a maximum with certain combinations of liquids because of the special spatial arrangement and interlocking of the various molecules in the complex resulting from their size, from the relative strengths of their affinity bonds, etc., so that it is necessary in any explanation to consider the relative specific characters of the liquids and the colloidal substance.

With increase in the solvent power of the liquid mixtures for cellulose nitrate, the change in density increases and the sols become relatively less viscous.

The surface tensions of the organosols are either the same as or slightly higher than that of the pure dispersion medium.

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CCCCVIII.—*The Allotropy of Zinc.*

By DAVID STOCKDALE.

THE work here described was undertaken in order to discover some sure means of recognising allotropy in metals at high temperatures and of accurately determining those temperatures. The experiments of other workers, those in which *X*-rays were used being left out of account, may be divided into two groups :

(*a*) Investigations of the physical properties of the metal, quenched from temperatures above and below that of the suspected transformation point.

(*b*) Experiments carried out in the neighbourhood of the transition point.

Objection to the former experiments can be made on three grounds :

(1) There is no certainty that, during the quenching, an allotropic metal does not revert to its original form.

(2) During the chilling of even a small specimen very great stresses are created, and these may cause false results to be obtained.

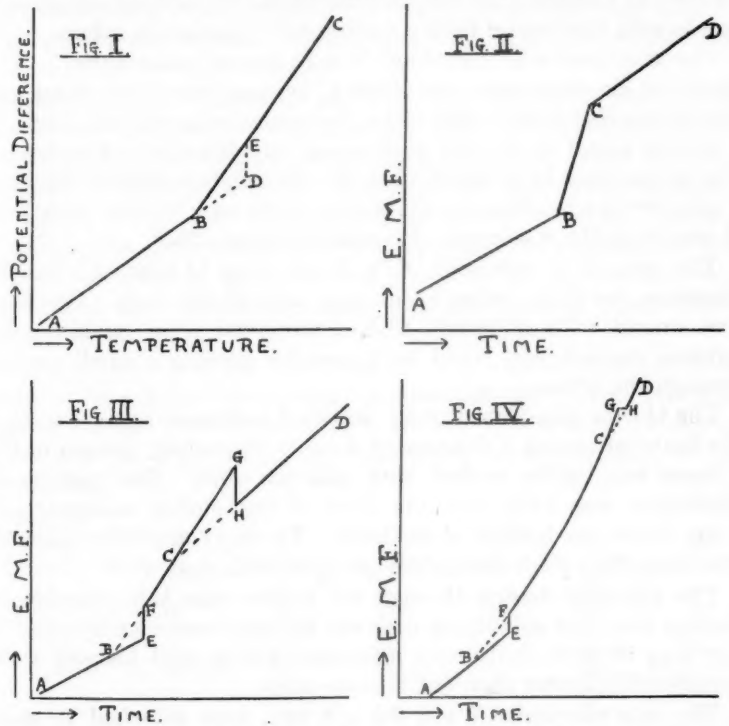
(3) Very little is known about the phenomena of " lag " in allotropic changes at high temperatures. It is possible that this lag may be so great that the temperature may be raised considerably above that of the transformation without any change taking place in the metal.

The third criticism can be made of the latter group of experiments also, which have consisted, for example, in investigations into the specific heats of metals at high temperatures, measurements of electrical resistance, of thermal electric power, and of the mechanical properties of the materials, but the most serious objection is that these methods are not infallible. For example, it has been shown by Miss Bingham (*J. Inst. Metals*, 1920, **24**, 333)—and confirmed by the author—that zinc undergoes an allotropic change between 310° and 330°; yet of all the physical properties of zinc, only the electrical resistance and the " mechanical " properties are definitely discontinuous through that range of temperature. Miss Bingham has shown that in the case of zinc the change in resistance is extremely small in comparison with the resistance. Attempts to carry out exact measurements with an ordinary tensile testing-machine would probably be futile.

The problem to be solved was to devise some method of measuring the change in a property of a metal in such a way that this change would appear large with respect to the quantity measured just prior to the transformation.

There is between a metal and an electrolyte in contact with it a certain difference of potential, which is a function of the temperature. If the potential difference and the temperature be plotted, the result may be a curve similar to A B (Fig. I). At the triple point (α-allotrope, β-allotrope, vapour) the solution pressure of the two forms must be the same, and therefore, if B represents the triple point, B must also lie on the potential difference–temperature curve (B C) of the β-allotrope. But there seems to be no reason why the slope of A B and of B C should be the same, and if exact measurements of

differences of potential could be made, triple points of metals which exhibit allotropy could probably be detected by changes in direction of the curve. The effect would be increased by "lag"; that is to say, one form might exist in a metastable condition over a range of temperatures and then suddenly change into the other. If such were the case, the curve would be of the form A B D E C and the triple point would be found by producing C E until it cut A D. By the use of this principle, Cohen (*Z. physikal. Chem.*, 1894, **14**, 53; see also Roozeboom, "Die Heterogenen Gleichgewichte vom Stand-



punkte der Phasenlehre," Vol. I, p. 123) was able to measure accurately the transition temperature of tin.

If a second electrode of the metal is immersed in the electrolyte, and connected with the first, a small, constant difference of temperature being maintained between them, an electrolytic cell will be formed having a very small *E.M.F.* The *E.M.F.*–temperature (or time) curve will be the algebraical difference between two curves such as A B C (Fig. I), and should have the form A B C D (Fig. II), B and C representing the temperatures at which the allotropic change takes place in the two electrodes. If allowance is made for

"lag," the theoretical curve should be of the form A B E F C G H D (Fig. III), and by producing the lines G F and D H the triple point should be ascertainable. The order of magnitude of the *E.M.F.* and of the changes in it can be made the same by choosing a suitable temperature difference between the two electrodes.

Experimental.

As it appeared certain, from the work of Miss Bingham, that zinc undergoes allotropic change at about 300°, it was thought advisable to test the foregoing theoretical conclusions by carrying out experiments with that metal before seeking such changes in others.

The zinc used was "Brunner Mond's purest electrolytic." The choice of an electrolyte was limited, because the liquid must not attack the zinc in any way, either by oxidation or by deposition of a second metal on it, and preliminary experiments had indicated that no gas must be given off when the electrolyte is heated. Finally, a mixture of zinc chloride, containing much oxychloride, with 10% of zinc bromide, was used. It melted at about 280°.

The apparatus consisted of a hard glass U-tube, 1·5 cm. in diameter, the limbs being 4 cm. apart and 22 cm. long. One limb was wound with nichrome ribbon protected from oxidation by pyruma cement, and could be heated by passing a small current through the ribbon.

The U-tube was placed in an electrical resistance furnace so that the limbs projected a distance of 5 cm.; the empty portion of the furnace was lightly packed with asbestos fibre. The quantity of electrolyte was such that the level of the molten material was 6 cm. above the bottom of the tube. To stop convection currents, the connecting piece was lightly plugged with glass wool.

The difficulty arising through the molten zinc salts running up the hot tube and solidifying near the top was overcome by winding the tops of both limbs with nichrome ribbon and keeping them considerably hotter than the bottom parts.

The zinc electrodes, 0·4 × 0·4 × 6 cm., were attached to stout copper wires passing through the rubber stoppers closing the limbs. The stoppers were also fitted with rubber valves, preventing access of atmospheric moisture. The copper wires were connected through a mirror galvanometer. In the circuit were a reversing key and an apparatus for opposing an *E.M.F.* to that generated by the little cell. The galvanometer threw a spot of light on a sheet of paper moving upwards at a uniform rate, and by following the spot of light with a pencil it was possible to draw an *E.M.F.*–time curve in a direct and easy way.

Temperatures were measured by copper–constantan couples

(size 30 gauge) sheathed in fine glass tubes, and so placed that the hot junctions were about 1 cm. above the bottoms of the electrodes. The couples were used in conjunction with millivoltmeters, standardised by means of the melting points of pure zinc, lead and tin.

Before a series of experiments was begun, the U-tube and its contents were heated to 400° to drive off any steam and to anneal the zinc. The tube was then heated or cooled at different rates through the range where the allotropic change might be expected to occur, the two limbs being kept at slightly different temperatures, and *E.M.F.*–time curves were drawn. An attempt was made to read the millivoltmetres every other minute.

The apparatus described above is unsatisfactory and the experimental difficulties are numerous. First, a single operator has too much to do if he is to obtain correct results. Then there are troubles with the electrolyte. It was found impossible to maintain a uniform temperature difference between the two limbs, and consequently the curves obtained were not sharp. As the galvanometer was not sufficiently sensitive, the breaks in the curves were very small, and were liable to be completely obscured by small experimental errors.

Sixteen curves in all were taken. The results obtained from eight of the more convincing experiments are in the following table : t is the time (mins.) taken for the temperature to change from 300° to 330°, and T the difference in temperature of the electrodes.

Type of curve.	T.	t.	E.	B.	G.	C.
Cooling.	6°	35	316°	318°	314°	316°
,,	15	30	—	—	308	—
,,	12	26	312	314	314	—
,,	7	Not obs.	312	314	308	313
Heating.	10	35	315	313	317	315
,,	6	30	316	—	315	315
,,	10	18	—	—	318	—
,,	10	7	328	—	318	—
			Mean	315		315

The letters above the columns refer to Fig. III. Blanks in the columns denote either that the position of the break was very doubtful or that the curve was of such a shape that it was impossible to find the point B or C accurately by interpolation.

Experiment 8, in which the rate of heating was fast, is interesting in that the lag in the hotter electrode was so great that the point F (Fig. III) lay between the points C and G, and the line F G was very short because the cooler electrode underwent the transformation almost immediately after the other.

The figures in columns B and C show that there is a transition point at 315°. It will be seen, also, that there is a "lag" at the rates of heating employed, but in no case was the measured "lag" very great. The largest values obtained were 7° below the mean temperature on cooling curves, and 13° above the mean temperature on heating curves. It is quite possible that this phenomenon of "lag" may have been responsible for the many failures to obtain breaks in the curves.

Fig. IV is an exact reproduction of the curve obtained in Experiment 4. In general, the others resembled it; in many cases, however, the observed breaks were much larger and sometimes they were not nearly so regular in shape.

Conclusion.

The experiments indicate that zinc undergoes allotropic change at 315°. This result agrees very well with those of Miss Bingham (*loc. cit.*), who found that changes occurred in some properties of zinc at about 330° and in others at about 310°.

The figures set out in the table seem convincing; the curves from which these figures are derived are not convincing, and the value 315° is to be accepted only with reserve.

The author regrets that circumstances have arisen which make it impossible for him to continue this work. His conviction that the principle underlying his experiments is correct and that a further attempt to apply it both to the examination of zinc and of other metals will yield valuable results, is his excuse for offering this paper for publication. In his opinion it is necessary to provide some means of confirming the existence of allotropic changes revealed by the use of *X*-rays.

The author expresses his gratitude to Mr. C. T. Heycock, M.A., F.R.S., for his interest and help, and to the Royal Commissioners of the Exhibition of 1851 for a senior studentship.

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CCCCIX.—*Electrometric Study of the Reactions between Alkalis and Silver Nitrate Solutions.*

By HUBERT THOMAS STANLEY BRITTON.

PRECIPITATES formed by the addition of alkalis to metallic salt solutions are, as a rule, basic. Silver oxide, however, appears to be an exception and therefore its precipitation by sodium hydroxide has been studied.

The precipitation of silver oxide from silver nitrate solution by ammonia and its subsequent re-solution have been studied from various points of view. Prescott (*Chem. News*, 1880, **42**, 31), Reychler (*Ber.*, 1883, **16**, 990), Draper (*Pharm. J.*, 1886, **17**, 488), and Herz (*Z. anorg. Chem.*, 1910, **67**, 248) found that when approximately 2 mols. of ammonia were added to 1 mol. of silver nitrate the precipitate formed redissolved. That the substances in these proportions do enter into some kind of reaction has been shown by the following physicochemical methods: cryoscopy and conductivity (Reychler, *Ber.*, 1883, **16**, 2421; 1895, **28**, 555), measurements of partial pressure of ammonia (Konowalov, *Z. physikal. Chem.*, 1898, **28**, 558; Gans, *Z. anorg. Chem.*, 1900, **25**, 236), thermochemical measurements (Berthelot and Delépine, *Compt. rend.*, 1899, **129**, 326; Bruni and Levi, *Gazzetta*, 1917, **47**, i, 259), and transference number determinations (Whitney and Melcher, *J. Amer. Chem. Soc.*, 1903, **25**, 70). The current view that silver exists in ammoniacal solutions as a complex kation, each silver atom being associated with two molecules of ammonia, originated in the work of Bodländer and Fittig (*Z. physikal. Chem.*, 1901, **39**, 597), who showed by an application of the mass law that the solubility of silver chloride in ammonia could be accounted for if the silver were assumed to pass into a complex ion, $Ag(NH_3)_x$, the values of x actually varying from 1·67 to 2·22. Little appears to be known of the process of formation of the complex, and consequently the experiments described in the second portion of this paper have been performed.

Experimental.

1. *Electrometric Titration with the Silver Electrode of Silver Nitrate with Sodium Hydroxide.*

The precipitation of silver oxide was studied by means of the following concentration cell, the $Ag|N/10\text{-}AgNO_3$ serving as the standard half-element; the other silver electrode dipped in the solution which was being titrated:

$$Ag\left|N/10\text{-}AgNO_3\right|\begin{matrix}\text{saturated}\\ KNO_3\text{ solution}\end{matrix}\left|\begin{matrix}100\text{ c.c. of }0{\cdot}02M\text{-}AgNO_3\\ +\ x\text{ c.c. of }0{\cdot}1N\text{-NaOH}\end{matrix}\right|Ag.$$

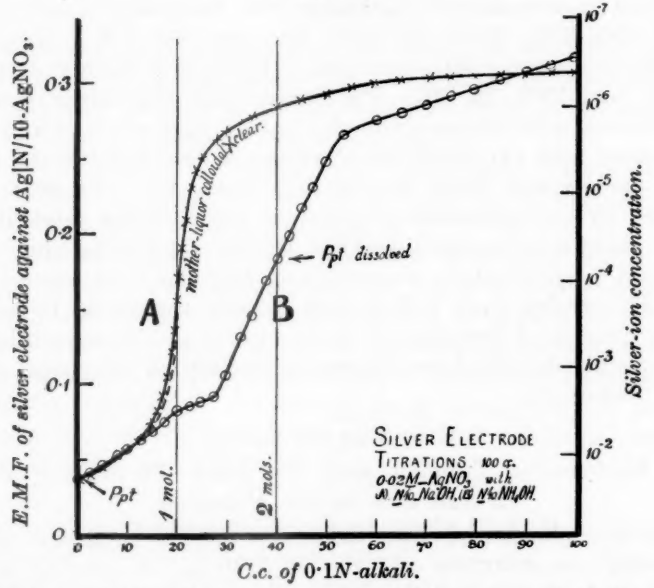
The alkali was added very slowly and before each measurement was made the mixture was thoroughly stirred. Steady and reproducible *E.M.F.*'s were readily obtained. The two electrodes, made from the same piece of silver wire, were fused into glass tubes so that lengths of 2 cm. were exposed, and covered electrolytically with layers of finely divided silver from silver nitrate solution. Checked against a normal calomel electrode, saturated potassium nitrate being used as junction liquid, they gave a normal electrode potential

of 0·802 volt at 20°, in good agreement with the accepted value, 0·80. *E.M.F.* of $Ag|N/10\text{-}AgNO_3|$Saturated $KNO_3|N$-Calomel = 0·456 volt. Therefore E_h of $Ag|N/10\text{-}AgNO_3$ = 0·739. The dissociation of silver nitrate in $N/10$-solution being taken as 81·4%, $E_h = 0{\cdot}739 = {}_oE_h + RT \log [Ag^{\cdot}]/nF = {}_oE_h - 0{\cdot}063$; and consequently ${}_oE_h =$ 0·802 volt. The results obtained are plotted in Fig. 1, curve A.

The precipitate formed during the addition of the first 10 c.c. of alkali was white, but immediately became brown. A little remained in colloidal suspension until 7 c.c. more than the theoretical amount of alkali had been added.

The dotted line (Fig. 1) represents the change in silver-ion con-

FIG. 1.



centration calculated on the assumption that precipitation had effected a proportional diminution in the silver-ion concentration of the mother-liquor. The observed and the theoretical curves are coincident for the first 15 c.c. of alkali, but thereafter the dotted curve lies a little lower, which may be due to the carrying down of silver nitrate by the precipitate. Silver nitrate in the precipitate would tend to become a "solution link" (compare Thomas and Freiden, *J. Amer. Chem. Soc.*, 1923, **45**, 2522) and its presence would account for some silver oxide remaining in colloidal solution. Much of the undecomposed silver nitrate was readily attacked, as will be seen from the great change in silver-ion concentration which took place at the point corresponding to the stoicheiometrical

amount of sodium hydroxide. There probably still remained a trace of unattacked silver nitrate, although too small to be shown in the diagram, for the colloidal solution was not decomposed until 7 c.c. excess of alkali had been added. This suggestion may account for the high initial values of the solubility product of silver hydroxide given in Table I. If the formation of such a colloidal solution is due to a stabilising influence, tending to increase the solubility of the dispersed particles, such as may be created by the silver oxide particles containing some undecomposed silver nitrate, it would be expected that silver hydroxide would be more soluble when a part of it is in colloidal solution than when it is not.

The silver-ion concentrations were calculated from the equation $E_{obs.} = -0{\cdot}063 - 0{\cdot}058 \log [Ag^{\cdot}]$, and the hydroxyl-ion concentrations from the excess of alkali added, complete dissociation being assumed. On introducing corrections for dissociation, the solubility products are diminished by about $0{\cdot}1 \times 10^{-8}$ in every case.

TABLE I.

v = cc. of 0·1*N*-sodium hydroxide added.

v.	*E.M.F.*	[Ag·] $\times 10^7$.	[OH′] $\times 10^4$.	[Ag·][OH′] $\times 10^8$.	v.	*E.M.F.*	[Ag·] $\times 10^7$.	[OH′] $\times 10^4$.	Ag·][OH′] $\times 10^8$.
20·5	0·171	925	4·15	3·84	35·0	0·279	12·7	111	1·41
21·0	0·191	418	8·26	3·45	40·1	0·285	9·98	143	1·43
22·0	0·208	212	16·4	3·48	50·1	0·293	7·46	200	1·49
23·0	0·231	85·3	24·4	2·08	60·0	0·300	5·51	250	1·38
24·0	0·241	57·3	32·3	1·85	71·1	0·303	4·89	289	1·46
25·0	0·250	40·2	40·0	1·68	80·0	0·303	4·89	333	1·63
27·62	0·263	24·0	59·4	1·43	90·0	0·3045	4·60	368	1·70
30·0	0·269	18·9	76·9	1·45	100·0	0·306	4·35	400	1·74

The average value of [Ag·][OH′] is $1{\cdot}51 \times 10^{-8}$ for the last ten determinations and $1{\cdot}44 \times 10^{-8}$ for values of v from 27·62 to 71·1. Böttger (*Z. physikal. Chem.*, 1903, **46**, 521) found the value $1{\cdot}52 \times 10^{-8}$ from conductivity measurements at 20°, and Jellinek and Gordon (*ibid.*, 1924, **112**, 212) the lower values $5{\cdot}5$ and $7{\cdot}3 \times 10^{-9}$ from *E.M.F.* measurements of $Ag|Ag_2O,x$NaOH. The cause of the discrepancy between these two results, and of their exceptional lowness, can be traced to the erratic behaviour of the silver electrode in presence of silver oxide in alkaline solutions, which Luther and Pokorný (*Z. anorg. Chem.*, 1908, **57**, 290) and Buehrer (cited in Lewis and Randall's "Thermodynamics," 1923, p. 483), who observed it, are inclined to attribute to reduction of the silver oxide at the expense of the electrode.

The behaviour of the $Ag|Ag_2O$,NaOH electrode during the titration may perhaps best be studied from a consideration of the voltages of the oxygen–hydrogen cell, as several attempts have been made to arrive practically at its *E.M.F.* through measurements

of the silver electrode in question. Nernst and Wartenberg (*Z. physikal. Chem.*, 1906, **56**, 534) found, by extrapolation from the results obtained in their classical researches on the dissociation of steam at high temperatures, that the potential difference of the oxygen–hydrogen cell at the ordinary temperature could be calculated from the expression $E.M.F. = 1{\cdot}232 - 0{\cdot}00085\ (t° - 17)$, and therefore the *E.M.F.* at 20° should be 1·229 volts. G. N. Lewis (*J. Amer. Chem. Soc.*, 1906, **28**, 158) calculated that the *P.D.* of $O_2|NaOH,Ag_2O|Ag$ is 0·049 volt at 25° from the dissociation pressures of silver oxide at high temperatures, which have since been confirmed by Keyes and Hara (*ibid.*, 1922, **44**, 479), the essential assumption being that no allotropic change in the silver oxide takes place on heating. Hence, the *E.M.F.* of $O_2| - |H_2$ being 1·229 volts at 20°, and calculation showing that the *E.M.F.* of $O_2|NaOH,Ag_2O|Ag$ at 20° is the same as at 25°, the *E.M.F.* of $Ag|Ag_2O,NaOH|H_2$ should be 1·180 volts at 20°. Using Böttger's value of the solubility product of silver hydroxide at 25°, Lewis calculated that the *P.D.* at 25° of the last combination should be 1·168 volts, and consequently that of the oxy-hydrogen cell should be 1·217 volts. Converted by means of the temperature coefficient given in Nernst and Wartenberg's equation, these *P.D.*'s become 1·172 and 1·221 volts at 20°, respectively. Luther and Pokorný (*loc. cit.*) found by direct experiment that the initial voltage of $Ag|Ag_2O$(electrolytically prepared),$NaOH|H_2$ was 1·172 volts at 25° (*i.e.*, 1·176 volts at 20°).

Table II gives the *P.D.*'s of the $Ag|Ag_2O,NaOH|H_2$ combination calculated for various stages of the titration, from which the *E.M.F.*'s of the oxygen-hydrogen cell were obtained by adding 0·049 volt (*vide supra*).

TABLE II.

C.c. of *N*/10-NaOH.	E_h $Ag\|Ag_2O,NaOH.$	E_h $H_2\|NaOH.$	*E.M.F.* $Ag,Ag_2O,NaOH\|H_2.$	*E.M.F.* $O_2\| - \|H_2.$
20·5	0·568	−0·621	1·189	1·238
22·0	0·531	−0·655	1·186	1·235
25·0	0·489	−0·681	1·167	1·216
30	0·470	−0·700	1·170	1·219
40	0·450	−0·710	1·164	1·213
60	0·439	−0·724	1·163	1·212
80	0·436	−0·731	1·167	1·216
90	0·435	−0·735	1·170	1·219
100	0·433	−0·736	1·169	1·218
			Mean 1·167	1·216

The E_h of $Ag|Ag_2O,NaOH$ was found by subtracting the observed voltages given in Table I from 0·739, the E_h of $Ag|N/10\text{-}AgNO_3$, it being assumed that the junction of saturated potassium nitrate solution reduced the diffusion potential to negligible dimensions.

The E_h's of the hydrogen electrode in alkaline solutions were calculated from the formula $E_h = 0{\cdot}0581 \log [H^+]$, K_w at 20° being $10^{-14{\cdot}07}$, and the sodium hydroxide being regarded as completely dissociated. On correcting for ionisation, the values become 2 to 3 millivolts less negative.

The first two *P.D.*'s of the oxygen–hydrogen cell are greater than the value, 1·229 volts, found by Nernst and Wartenberg (*loc. cit.*). The discrepancy may be due to a slightly increased solubility of the silver oxide through some having been in colloidal solution, and possibly also to some extent to the fact that precipitation had only just ended and consequently any reduction which might have taken place would be at a minimum.

Save for the first two values, the *E.M.F.*'s of the $Ag|Ag_2O,NaOH|H_2$ range from 1·163 to 1·170 volts. The average value, 1·167 volts, is 13 millivolts less than the one given by Nernst and Wartenberg, 5 mv. less than that of Lewis, and 9 mv. less than the initial value of Luther and Pokorný for electrolytic silver oxide.

Rørdam (*Z. physikal. Chem.*, 1921, **99**, 474) has determined the *P.D.*'s of many cells, $Ag|Ag_2O,alkali|H_2$, in which both barium and sodium hydroxides were employed and also samples of silver oxide which had been subjected to a variety of treatments. With precipitated oxides, the *E.M.F.*'s varied from 1·137 to 1·155 volts at 25°, or from 1·141 to 1·159 at 20°, the higher values being obtained with those oxides which had not been separated from the solutions from which they were precipitated. On the other hand, by electrolysing a sodium hydroxide solution between a platinised platinum kathode and a silver anode, he found that, after the current had been flowing for a few minutes, the *E.M.F.* measured immediately after it was stopped varied between 1·171 and 1·177 volts at 25° (*i.e.*, 1·175 to 1·181 volts at 20°), the kathode becoming in effect a hydrogen electrode. The highest value agreed with the value extrapolated from the work of Nernst and Wartenberg and Lewis.

The values given in Table II of the *E.M.F.*'s of the $Ag|Ag_2O,NaOH|H_2$ fall between those indicated by Rørdam's measurements. It is significant that the highest value for precipitated oxides, corresponding to 1·159 volts at 20°, indicated by Rørdam's work was obtained with silver oxide which had not been removed from the solution in which it was precipitated. The higher *E.M.F.*'s of the present author may be due to the fact that they were measured within a few moments of precipitation. If the lowness of the $Ag|Ag_2O,NaOH$ results is due, as suggested by Buehrer and Luther and Pokorný, to reduction, it would appear that the higher values obtained in this work were due to reduction having taken place to a smaller extent than in the experiments of Rørdam.

Strangely enough, Rørdam attributed the low results given by precipitated oxides, as compared with those given by the electrolytic oxide, to the existence of two different modifications of silver oxide, having different dissociation pressures, and by means of the Nernst heat theorem he calculated the transformation temperature to be 132°. For the purpose of calculation, he took 1·143 volts at 25° to be the *E.M.F.* of

$$Ag|Ag_2O(precipitated),NaOH|H_2$$

in spite of the wide variation in his experimental values, *viz.*, from 1·137 to 1·155. He considered that the precipitated oxides were the forms stable below 132° and that the electrolytic oxide was metastable at the ordinary temperature but stable above 132°. For this reason, the method adopted by Lewis in his calculation of the *P.D.* of $O_2|NaOH,Ag_2O|Ag$ was held to be inadmissible. This hypothesis does not account for the *E.M.F.*'s found in this work, which, as already stated, lie between those obtained with the two supposed forms of silver oxide. The variable results obtained with the $Ag|Ag_2O$,alkali electrode, especially after standing for some time, appear to be best accounted for by reduction. The low solubility products obtained by Jellinek and Gordon (*loc. cit.*) were probably due to this cause, especially if the exceptionally low values of the extrapolated *P.D.*'s of the $Ag|Ag_2O,NaOH|H_2$ cell be considered, in one case 1·150 volts at 20° and in another 1·139.

TABLE III.

Temp.	Method.	Mols. AgOH per litre $\times 10^4$.	$[Ag^{\cdot}][OH']$ $\times 10^8$.	Observer.
20°	Analysis.	1·48—1·85	2·2—3·4	Whitby, 1910.
	Conductivity.	1·23	1·52	Böttger, 1903.
	E.M.F.	0·7—0·9	0·6—0·7	Jellinek and Gordon, 1924.
	,,	1·2	1·5	Britton, this paper.
	Calculation.	1·67	2·78	,, ,,
25°	Analysis.	1·73—2·26	3·0—5·1	*Noyes and Kohr, 1902.
	,,	4·3—5·9	18·6—34·9	†Rebière, 1915.
	Equilibria.	1·5	2·25	Noyes and Kohr, 1902.
	,,	1·8	3·2	Abegg and Cox, 1903.
	Conductivity.	1·39	1·93	Böttger, 1903.
	E.M.F.	0·95	0·9	‡Calc. from the data of Abegg and Cox, 1903.
	Calculation.	1·66	2·74	Britton, this paper.

* *J. Amer. Chem. Soc.*, 1902, **42**, 336.

† Rebière's values (*Bull. Soc. chim.*, 1915, **17**, 309) are probably twice too high, for he states that his lowest value agrees with Noyes's average value.

‡ Rørdam showed that the *E.M.F.* of $Ag|Ag_2O,N/10\text{-}Ba(OH)_2|H_2$ (compare Abegg and Cox, *Z. physikal. Chem.*, 1903, **46**, 1) on which this calculation was based was 1·140 volts, thereby accounting for the low value of the solubility product.

The solubility products given in Table I, when considered in connexion with the *E.M.F.*'s of the $Ag|Ag_2O,NaOH|H_2$ combination, appear to be lower than would be expected from the fundamental calculations of Nernst and Wartenberg and Lewis. Had the electrode been satisfactory, the potential difference of the combination should have been $1{\cdot}229 - 0{\cdot}049 = 1{\cdot}180$ volts at 20°, from which it follows that $[Ag^{\cdot}][OH'] = 2{\cdot}78 \times 10^{-8}$ at 20°. The theoretical potential difference of $Ag|Ag_2O,H_2O|H_2$ at 25° is 1·176 volts, which gives $[Ag^{\cdot}][OH'] = 2{\cdot}74 \times 10^{-8}$ at that temperature.

Analytical determinations of the solubility of silver oxide have given widely differing results, which were dependent on the length of time allowed for the attainment of equilibrium and on the method of preparation of the oxide. Whitby (*Z. anorg. Chem.*, 1910, **47**, 107) found that at 20° silver oxide required 14 days to attain equilibrium with water. Table III gives a comparison of the results obtained at 20° and 25° by chemical and physical methods. The solubility products have been calculated on the assumption that the dissolved silver oxide was completely ionised.

At both temperatures the data obtained by direct analysis are higher than those obtained by physical methods. This may perhaps be partly due to incomplete dissociation of the silver oxide. The variable results obtained by *E.M.F.* methods show that these are unsatisfactory. The author's value at 20° is probably low and yet agrees with that of Böttger. Böttger's value at 25° was used by Lewis in his fundamental calculation of the *E.M.F.* of the oxygen–hydrogen cell, and, contrary to the contention of Rørdam, the low value he obtained is probably thus accounted for.

2. *Electrometric Titrations of Silver Nitrate with Ammonium Hydroxide by means of* (a) *the Oxygen Electrode, and* (b) *the Silver Electrode.*

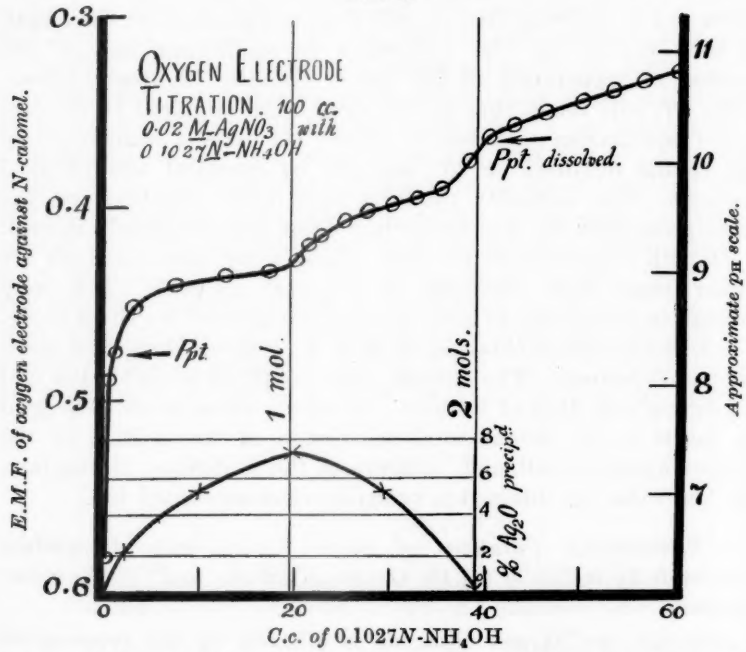
Although the oxygen electrode is affected by the presence of silver oxide, it can be used to indicate any pronounced changes in hydrogen-ion concentration which may take place when alkalis are added to silver salt solutions (this vol., p. 2148). The change in hydrogen-ion concentration occurring during the formation of the silver ammonia complex from silver nitrate and ammonia has therefore been followed with its aid.

0·02*M*-Silver nitrate (100 c.c.) was titrated with 0·1027*N*-ammonium hydroxide at 18°, the oxygen electrode and the normal calomel electrode being used with saturated potassium nitrate solution as junction liquid. In Fig. 2, the observed *E.M.F.*'s are plotted against the quantities of ammonia added. The proportional hydrion scale affixed to the diagram is based on colorimetric

measurements, by Gillespie's drop-method (*J. Amer. Chem. Soc.*, 1920, **42**, 742), of the hydrion concentrations of the solution at the beginning and the end of the titration. The scale showed hydrion concentrations at various stages of the titration which were in accord with those given by indicators.

The curve shows that the first drop of ammonia produced a sudden increase in p_H and that precipitation began when 1 c.c. had been added. The addition of more ammonia caused a further diminution in hydrogen-ion concentration until the p_H (approx. 9)

FIG. 2.



was reached at which silver oxide is normally precipitated. The change thereafter was a gradual one, until 1 mol. of ammonia (per mol. of silver nitrate) had been added; a small but definite inflexion then occurred, and was followed by another when 2 mols. of ammonia had been added. At this stage the precipitate had completely dissolved. Draper (*loc. cit.*) noted that solutions containing the reactants in these proportions were strongly alkaline to turmeric and phenolphthalein, *i.e.*, above p_H 8.

It might be imagined from the nature of the curve that the first section, corresponding to the addition of the first mol. of ammonia, represents the complete precipitation of silver oxide, and the second section its reaction with one mol. of ammonia to form a soluble

monoammino-silver complex. The precipitation, however, was far from complete during the first part; and if a little, but sufficient, nitric acid had been added to a silver nitrate solution treatment with ammonia produced no precipitate. Moreover, moist silver oxide is readily soluble in ammonium nitrate solution, and in an amount that suggests the formation of $AgNO_3,NH_3$. The silver oxide precipitated on mixing equal volumes of $N/10$-silver nitrate and $N/10$-sodium hydroxide dissolved completely at room temperature in quantities of $N/20$-ammonium nitrate corresponding to the ratios 1 mol. AgOH : 1·1—1·2 mols. NH_4NO_3. The solutions had p_H about 8 and did not decompose on boiling. The silver-ion concentration of the solutions was comparatively large, *e.g.*, a solution composed of 20 c.c. of $0{\cdot}1N$-sodium hydroxide, 20 c.c. of $0{\cdot}1N$-silver nitrate, and 45 c.c. of $0{\cdot}05N$-ammonium nitrate contained 33·5% of the total silver present as silver ions. This may have been due to the presence of a highly dissociated monoammino-silver complex or of some silver nitrate and some diammino-complex.

Reychler (*Ber.*, 1883, **16**, 990) and Draper (*loc. cit.*) found that ammonia, if added in small quantities, caused partial precipitation of silver oxide from silver nitrate solution. In order to study this reaction more fully, the percentage amounts of silver oxide precipitated at different stages of the titration were determined. The results are in Table IV, and are shown diagrammatically in Fig. 2.

TABLE IV.

C.c. of $0{\cdot}1027N$-NH_4OH.	Mols. NH_4OH/ Mols. $AgNO_3$.	Ag_2O pptd. %.	Ppted. Ag_2O as percentage of the amount theor. precipitable.
1·95	0·1	2·2	22·0
9·8	0·5	5·3	10·6
19·5	1·0	7·3	7·3
29·3	1·5	5·3	
39·0	2·0	0	

No precipitation with ammonia occurred when the solution contained nitric acid in quantities greater than 0·05 mol. for 1 mol. of silver nitrate.

It appears that, although the solution had attained the p_H necessary for the precipitation of silver oxide, another reaction was taking place which withdrew from the solution some of the silver ions that ordinarily would have been precipitated. This may be seen from curve B in Fig. 1, which represents the titration of 100 c.c. of $0{\cdot}02M$-silver nitrate with $N/10$-ammonia with the aid of the silver electrode, carried out at 18° in the same way as the sodium hydroxide titration. The portions of the curves A and B corresponding to the addition of the first 15 c.c. of alkali are almost identical in spite of the partial precipitation produced by the ammonia. This

indicates that silver ions were being removed from solution mainly owing to complex formation. A small inflexion occurred when 1 mol. of ammonia had been added. Calculation from the data of Figs. 1 and 2 shows that the product $[Ag^{\cdot}][OH']$ became less and less during the addition of the second molecule of ammonia; when the addition was complete, its value was $0{\cdot}6 \times 10^{-8}$, which is less than the solubility product of silver hydroxide and thus accounts for the re-solution. The main inflexion occurred when 2 mols. of ammonia had been added. Bruni and Levi (*Gazzetta*, 1917, **47**, i, 259) made, among their measurements with the silver electrode, four on solutions containing less than 2 mols. of ammonia for 1 mol. of silver nitrate. Their results show that a sharp diminution in silver-ion concentration takes place when between 1·5 and 2 mols. of ammonia have been added.

The inflexion (Fig. 2) which occurred when 1 mol. of ammonia had been added may probably be accounted for by the fact that at that point the precipitation reaction stopped, and consequently the destruction of hydroxyl ions ceased. The slight inflexion in the silver-ion curve (B, Fig. 1) may be due to the two reactions, taking place during the addition of the first molecule of ammonia and causing precipitation and complex formation, being followed by complex formation only, which effects solution of the precipitate.

An attempt has been made to account for the silver-ion concentrations measured during the addition of the first 2 mols. of ammonia. The reactions were assumed to be (1) $AgNO_3 + NH_4OH \rightarrow AgOH + NH_4NO_3$, and (2) $AgNO_3 + 2NH_3 \rightleftharpoons Ag(NH_3)_2NO_3$. The amount of ammonia required for the precipitation of the silver oxide having been subtracted from the total amount of ammonia added, the remainder was regarded as having been converted entirely into the complex salt $Ag(NH_3)_2NO_3$. The concentration of silver nitrate originally present being known, the concentration of unchanged silver nitrate could be calculated. The results are in Table V. The concentrations of free ammonia given in the last column were calculated from the expression $[Ag^{\cdot}][NH_3]^2/[Ag(NH_3)_2^{\cdot}] = 2{\cdot}2 \times 10^{-8}$ (*vide infra*).

TABLE V.

NH_4OH added. C.c.	Mols. per mol. of $AgNO_3$.	Conc. of Ag ions found $\times 10^4$.	Ag_2O ppted. %	Conc. of $Ag(NH_3)_2NO_3$ $\times 10^4$.	Conc. of $AgNO_3$ $\times 10^4$.	Calc. conc. of free NH_3 $\times 10^4$.
2	0·1	170	2·2	7·6	180	0·21
10	0·5	85	5·3	41	130	1·0
20	1·0	30	7·3	77	77	2·4
30	1·5	12	5·3	110	34	4·5
40	2·0	0·57	0	140	0	23

It will be observed that the concentrations of silver ions and silver nitrate were of the same order, although the former became appreciably smaller as the quantity of added ammonia increased. The dissociation constant of ammonium hydroxide being taken as $2{\cdot}3 \times 10^{-5}$, the hydroxyl-ion concentration in equilibrium with the free ammonia present when 2 mols. had been added was $10^{-3{\cdot}64}$, and therefore p_H was 10·5, as compared with 10·2 shown by the scale in Fig. 2. If it be assumed that the concentration of ammonium nitrate in the solution when 1·5 mols. of ammonia had been added was equivalent to the amount of silver oxide precipitated, it can be shown that the amount of free ammonia, $4{\cdot}5 \times 10^{-4}$, should have produced p_H 9·3 (9·6; Fig. 2). The hydrogen-ion concentration prevailing in the earlier part of the titration was undoubtedly controlled by the hydroxyl ions originating from the precipitated silver oxide. The effect of a little nitric acid in a silver nitrate solution in preventing the precipitation of silver oxide with ammonia appears to be due to the depressing influence of the ammonium nitrate on the ionisation of the ammonium hydroxide.

It thus seems probable that the complex silver compound ultimately formed required 2 mols. of ammonia for its formation. The results in Table VI refer to the solutions which contained ammonia in excess of 2 mols. For the purpose of calculation, the ammonia in excess of 2 mols. was assumed to be in the uncombined state, the small dissociation of the ammonium hydroxide was disregarded, and the complex silver salt was taken as being completely dissociated thus: $Ag(NH_3)_2NO_3 \rightleftharpoons Ag(NH_3)_2^{\cdot} + NO_3'$. The data used are those represented graphically in curve B (Fig. 1), and the concentration of silver ions was calculated from the formula $E = -0{\cdot}063 - 0{\cdot}0577 \log [Ag^{\cdot}]$.

TABLE VI.

$NH_3/AgNO_3$.	C.c. of $N/10$-NH_4OH.	*E.M.F.*	$[Ag^{\cdot}]$.	$[Ag(NH_3)_2^{\cdot}] \times 10^1$.	$[NH_3]$.	$K = [Ag^{\cdot}][NH_3]^2/[Ag(NH_3)_2^{\cdot}] \times 10^8$.
2·26	45·1	0·217	$1{\cdot}40 \times 10^{-5}$	13·9	0·0035	1·26
2·5	50·0	0·248	$4{\cdot}07 \times 10^{-6}$	13·3	0·0067	1·36
3·0	60·0	0·275	$1{\cdot}39 \times 10^{-6}$	12·5	0·0125	1·74
3·5	70·0	0·286	$9{\cdot}0 \times 10^{-7}$	11·8	0·0177	2·38
4·0	80·0	0·295	$6{\cdot}3 \times 10^{-7}$	11·1	0·0222	2·78
4·5	90·0	0·307	$3{\cdot}8 \times 10^{-7}$	10·5	0·0263	2·50
5·0	100·0	0·317	$2{\cdot}6 \times 10^{-7}$	10·0	0·030	2·33
104	—	0·490	$2{\cdot}9 \times 10^{-10}$	9·5	0·971	2·90
					Mean	2·2

The values of K appear to confirm the existence of the diammino-silver compound in ammoniacal solutions. The first three low values of K refer to solutions in which a rapid change in silver-ion concentration was taking place, as shown in curve B (Fig. 1).

These values being omitted, the table shows that there is little variation in the constant, even although the molar ratio $NH_3/AgNO_3$ varies from 2 to 104. Calculation from Bruni and Levi's *E.M.F.* measurements (*loc. cit.*) shows not only that the silver-ion concentration in ammoniacal solutions becomes extremely small, but also that the constant K of the supposed complex kation is similar to that found above. They measured the *E.M.F.*'s of a series of cells of the type $Ag\left|\begin{matrix}N/10\text{-}AgNO_3\\ xN\text{-}NH_4OH\end{matrix}\right|N/10\text{-}NaNO_3\left|N/10\text{-Calomel}\right.$ (A) at 15°. The *E.M.F.* of the combination $Ag|N/10\text{-}AgNO_3|N/10\text{-}NaNO_3|N/10$-Calomel was 0·407 volt (B). The difference of the *E.M.F.*'s of A and B gives the *E.M.F.* of the concentration cell $Ag\left|\begin{matrix}N/10\text{-}AgNO_3\\ xN\text{-}NH_4OH\end{matrix}\right|N/10\text{-}NaNO_3\left|N/10\text{-}AgNO_3\right|Ag$, from which the concentrations of silver ions were found by means of $E = -0{\cdot}063 - 0{\cdot}0571 \log [Ag^{\cdot}]$. Table VII was compiled from the measurements of Bruni and Levi.

TABLE VII.

$NH_3/AgNO_3$.	$[Ag(NH_3)_2^{\cdot}]$.	Free NH_3.	*E.M.F.* against *N*/10-Cal.	$[Ag^{\cdot}]$.	$K=[Ag^{\cdot}][NH_3]^2/[Ag(NH_3)_2^{\cdot}]$ $\times 10^8$.
2·5	0·1	0·05	+0·111	$5{\cdot}8 \times 10^{-7}$	1·45
4·0	0·1	0·2	+0·049	$4{\cdot}9 \times 10^{-8}$	1·95
5·0	0·1	0·3	+0·029	$2{\cdot}2 \times 10^{-8}$	1·95
6·67	0·1	0·467	+0·002	$7{\cdot}6 \times 10^{-9}$	1·66
10	0·1	0·8	−0·017	$3{\cdot}4 \times 10^{-9}$	2·19
20	0·1	1·8	−0·055	$7{\cdot}6 \times 10^{-10}$	2·46
30	0·1	2·8	−0·077	$3{\cdot}0 \times 10^{-10}$	2·35
40	0·1	3·8	−0·093	$1{\cdot}6 \times 10^{-10}$	2·35
50	0·1	4·8	−0·107	$9{\cdot}6 \times 10^{-11}$	2·19
60	0·1	5·8	−0·119	$7{\cdot}6 \times 10^{-11}$	2·57
70	0·1	6·8	−0·129	$6{\cdot}2 \times 10^{-11}$	2·82
80	0·1	7·8	−0·138	$5{\cdot}0 \times 10^{-11}$	3·02
100	0·1	9·8	−0·156	$3{\cdot}5 \times 10^{-11}$	3·31
				Mean	2·3

Bruni and Levi's data refer to solutions, decimolar with respect to silver nitrate, but the ammonia content of which varied continuously from 0·25 to 10·0*N*. The results in Tables VII and VIII show that silver nitrate solutions varying in concentration from 0·0095*M* to 0·1*M*, when rendered ammoniacal from 2- to 100-fold, contain the $Ag(NH_3)_2^{\cdot}$ kation, the dissociation constant of which is $2{\cdot}2 \times 10^{-8}$ approximately. It is probable that the base $Ag(NH_3)_2OH$ is much stronger than ammonium hydroxide and consequently the salt $Ag(NH_3)_2NO_3$ exists in solution.

Bruni and Levi also measured the potential differences between a silver electrode immersed in various ammoniacal solutions of silver nitrite and a decinormal calomel electrode at 15°, using *N*/10-sodium nitrite as junction liquid. In view of the stability of

the diammino-silver kation when attached to the nitrate ion, the data on nitrite solutions were considered of especial interest in that they might serve to show the behaviour of the complex kation when combined with another anion. Its dissociation constant has been calculated and the results obtained are in Table VIII. The silver-ion concentrations were calculated from E (obs.) = 0·463 − 0·0571 log [Ag$^{\cdot}$], in which the ${}_{o}E_{h}$ of silver was taken as 0·800 volt, and E_h of N/10-calomel as 0·337 volt.

TABLE VIII.

$NH_3/AgNO_3$.	$[Ag(NH_3)_2^{\cdot}]$.	Free NH_3.	*E.M.F.* against N/10-Cal.	[Ag$^{\cdot}$].	$K=[Ag^{\cdot}][NH_3]^2/[Ag(NH_3)_2^{\cdot}]$ $\times 10^8$.
2·5	0·02	0·01	+0·169	$6·9 \times 10^{-6}$	3·46
4·1	0·02	0·0407	+0·098	$4·1 \times 10^{-7}$	3·37
5	0·02	0·060	+0·076	$1·7 \times 10^{-7}$	2·99
6·7	0·02	0·0933	+0·041	$4·1 \times 10^{-8}$	1·77
10	0·02	0·160	+0·019	$1·7 \times 10^{-8}$	2·17
20	0·02	0·360	−0·019	$3·6 \times 10^{-9}$	2·36
30	0·02	0·559	−0·043	$9·8 \times 10^{-10}$	1·52
40	0·02	0·760	−0·055	$8·7 \times 10^{-10}$	2·52
50	0·02	0·960	−0·065	$5·6 \times 10^{-10}$	2·59
				Mean	2·5

The results in Table VIII show that the silver-ion concentrations in ammoniacal solutions of silver nitrite are due to the dissociation of a diammino-silver complex, the dissociation constant of which is $2·5 \times 10^{-8}$, and is therefore independent of the anion.

Kohlschütter and Fischmann (*Annalen*, 1912, **387**, 94) made some electrometric determinations on ammoniacal solutions of silver nitrate, but their data, on calculation, fail to give any constancy for K. The only other solutions in which the existence of the complex kation has been established by proving that K is a constant are ammoniacal solutions of silver chloride, which Bodländer and Fittig (*Z. physikal. Chem.*, 1902, **39**, 597) found to give K equal to $7·88 \times 10^{-8}$, and ammoniacal solutions of silver oxide, for which Euler (*Ber.*, 1903, **36**, 1854, 2878) obtained values of K ranging from 3·4 to $6·4 \times 10^{-8}$ at 16° when the ammonia was in large excess, and from 1·5 to $1·67 \times 10^{-8}$ when the excess was small.

Summary.

(1) The precipitation of silver oxide with sodium hydroxide has been studied electrometrically, and the solubility product [Ag$^{\cdot}$][OH$'$] calculated.

(2) The behaviour of the silver electrode in alkaline solutions containing suspended silver oxide has been discussed, and Rørdam's view that two modifications of silver oxide exist shown to be improbable.

(3) The value of the *E.M.F.* of the oxygen–hydrogen cell

found by Lewis is low, probably because a low value was taken for $[Ag^{\cdot}][OH']$.

(4) The reaction between silver nitrate and ammonia has been studied and further evidence of the existence of the complex kation $Ag(NH_3)_2^{\cdot}$ obtained.

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IMPERIAL COLLEGE OF SCIENCE AND TECHNOLOGY,
LONDON. [*Received, August 14th*, 1925.]

NOTES.

Preparation of p-*Bromophenylhydroxylamine by the Emulsification Process. A Modification.* By ROBERT DOWNS HAWORTH and ARTHUR LAPWORTH.

IT has been found that the reduction of pure *p*-bromonitrobenzene is often quite unsuccessful if carried out as previously described (J., 1921, **119**, 770). The following modification of the original method, however, usually gives a yield of *p*-bromophenylhydroxylamine nearly the same as that originally obtained but involves the use of more solvent benzene and preferably also more reducing solution. It is essential that the sodium sulphide crystals used in making the reducing solution should be of good quality.

p-Bromonitrobenzene (5 g.), benzene (40 c.c.), the hydrosulphide solution (120 g., prepared as formerly described, *loc. cit.*, p. 769), and calcium chloride (5 g., in a little water) are emulsified. Crystals soon separate and, after 1½ hours, solid ammonium chloride (5 g.) is added, the whole shaken, and the precipitated *p*-bromophenylhydroxylamine (about 2·9 g.) collected and washed with water. The benzene layer of the filtrate is separated, washed with water, dried over anhydrous sodium sulphate, and carefully diluted with petroleum (b. p. 40—60°); a further crop (about 0·5 g.) of the hydroxylamine is then obtained.

Three experiments carried out in the above way gave total yields of 2·7 g., 3·4 g., and 3·3 g., respectively, of *p*-bromophenylhydroxylamine. With the smaller quantity (52 g.) of sodium hydrosulphide solution previously advised, the yields in five experiments were 2·4—3·2 g.—THE UNIVERSITY, MANCHESTER. [*Received, November 24th*, 1925.]

Action of Hydrazine Hydrate on Phenanthraquinone. A Correction.
By SIKHIBHUSHAN DUTT.

IT was stated by Dutt and Sen (J., 1923, **123**, 3420) that phenanthrone is the sole product obtained from phenanthraquinone by the action of hydrazine hydrate. In subsequent experiments with commercial hydrazine hydrate (50%) 9 : 10-dihydroxyphenanthrene (m. p. 147°) was almost exclusively obtained instead of phenanthrone.

Fortunately, a small quantity of the original "hydrazine hydrate" in a sealed tube was available and this was found to be incorrectly labelled, the substance being actually pure anhydrous hydrazine. Further experiments have shown that, when anhydrous hydrazine is allowed to react with phenanthraquinone in absolute alcohol, phenanthrone is obtained in good yield and that, when small quantities of moisture are present or when ordinary commercial hydrazine hydrate is employed, 9 : 10-dihydroxyphenanthrene is almost the sole product.

The error was made through unavoidable circumstances, but is none the less regretted.—IMPERIAL COLLEGE, SOUTH KENSINGTON, S.W. 7. [*Received, November 28th*, 1925.]

The Aluminioxalates of some Optically Active Bases. By THOMAS BRUCE CHILD, ELWYN ROBERTS, and EUSTACE EBENEZER TURNER.

COMPOUNDS of the aluminioxalate type, derived from the acid $H_3Al(C_2O_4)_3$, should be capable of resolution into optically active forms. This has been attempted by means of active bases.

Strychnine Aluminioxalate.—Barium aluminioxalate (Burrows and Walker, J., 1923, **123**, 2738) twice crystallised from water was warmed with the calculated quantity of aqueous strychnine sulphate. The precipitate of barium sulphate and strychnine aluminioxalate was extracted with boiling water, and the extract allowed to crystallise. Different crops had $[\alpha]_D^{20°}$ −24·0° to −21·0° in 50% aqueous acetone, and formed slender, colourless needles, very sparingly soluble in water [Found : strychnine, 63·0; C_2O_4, 16·6. $(C_{21}H_{22}O_2N_2)_3,H_3Al(C_2O_4)_3,16H_2O$ requires strychnine, 63·4; C_2O_4, 16·7%]. When these salts were recrystallised, partial decomposition occurred with formation of strychnine oxalate and aluminium hydroxide, and no conclusions can be drawn in connexion with any rotational differences observed.

When a solution of sodium aluminioxalate was treated with half its equivalent of aqueous strychnine hydrochloride a salt was obtained which had $[\alpha]_D^{20°}$ −19·0° in 50% aqueous acetone. It was treated with aqueous potassium iodide, and the precipitated strych-

nine hydriodide removed. The resulting solution of potassium aluminioxalate contained a trace of colloidal aluminium hydroxide, and what optical measurements were possible pointed to the inactivity of the solution.

Crystallisation of strychnine aluminioxalate from acetone gave crops of salt having slightly different specific rotations, but consistent results could not be obtained.

l-*Menthylamine Aluminioxalate.*—The barium salt was digested at 100° with an aqueous solution of the equivalent quantity (10 g.) of *l*-menthylamine, previously dissolved in the calculated quantity of dilute sulphuric acid. Sufficient water was added to keep all the menthylamine salt in solution, and after filtration from barium sulphate 17 g. of l-*menthylamine aluminioxalate* separated in well-defined prisms which were sparingly soluble in water [Found: *l*-menthylamine, 59·2; C_2O_4, 33·6. $(C_{10}H_{21}N)_3,H_3Al(C_2O_4)_3,H_2O$ requires *l*-menthylamine, 59·9; C_2O_4, 34·0%]. This salt had $[\alpha]_D^{20°}$ −28·5° in 50% aqueous acetone. Recrystallisation, which was accompanied by partial decomposition, gave no evidence of resolution.

Treatment of a concentrated solution of sodium aluminioxalate with one-third of the equivalent quantity of *l*-menthylamine sulphate gave a salt having a rotation practically identical with the above.

l-*Phenylethylamine Aluminioxalate.*—This salt was prepared by digesting the barium salt with the calculated quantity of aqueous *l*-phenylethylamine sulphate at 100° for about an hour, removing the barium sulphate, and evaporating to a small bulk under diminished pressure. It crystallised from water, in which it was very soluble, in colourless prisms. The main bulk of the salt had $[\alpha]_D^{20°}$ −3·00° in aqueous solution [Found: C_2O_4, 39·1.

$$(C_8H_{11}N)_3,H_3Al(C_2O_4)_3,H_2O$$

requires C_2O_4, 39·1%]. After it had been recrystallised four times from water, its rotation was not measurably affected (Found: *l*-phenylethylamine, 53·0; C_2O_4, 39·2. Calc., *l*-phenylethylamine, 53·7%).

Distrychnine potassium aluminioxalate and d-*phenylethylamine dipotassium aluminioxalate* were also prepared. Their specific rotations did not change as a result of repeated recrystallisation. *Cinchonidine aluminioxalate* was obtained as a gummy solid which could not be crystallised.

The authors wish to thank the Research Fund Committee of the Chemical Society for a grant by means of which the expense of this work has been met.—East London College, University of London. [*Received, September 19th,* 1925.]

OBITUARY NOTICES.

RICHARD BURTLES.

BORN MAY 25TH, 1900; DIED JULY 3RD, 1925.

RICHARD BURTLES was the younger son of the late Alderman Richard Burtles of Manchester. He was educated at Manchester Grammar School, and at the College of Technology, Manchester. He obtained the B.Sc. Tech. degree in July, 1921, being placed in the first (Honours) division, and was awarded a Manchester Education Committee Research Scholarship. This enabled him to devote a year to research, during which he carried out an investigation on the tautomerism of the diphenylglyoxalines, by which he earned the M.Sc.Tech. degree. He was then given a maintenance grant by the Department of Scientific and Industrial Research, and investigated the preparation of 2-aminoglyoxalines and their behaviour towards nitrous acid. The patience, skill, and enthusiasm which he showed in these researches led to his appointment, in July, 1924, as the writer's research assistant. In January, 1925, he took a position as chemist to the Goodrich Rubber Company, Ltd., of Leyland, and held this position until his death, which was due to a bicycle accident.

Burtles was elected a Fellow of the Chemical Society in May, 1923, and published three papers, jointly with the writer, in the *Journal* (1923, **123**, 361; 1925, **127**, 581, 2012). He was greatly interested in stained glass, no doubt owing to the fact that his father had been a glass manufacturer, and contributed articles on "The Colouring of Mediæval Glass" and "The Decay of Ancient Glass" to the *Journal of the Manchester University Science Federation* (1923, **2**, i, 18; 1924, **2**, ii, 62). He took a useful part in the social life of the college, becoming Secretary of the Manchester University Science Federation and also of the College of Technology Chemical Society, and was very popular with the staff and students.

During his school career, Burtles underwent training for military service in the Officers Training Corps, and reached the rank of lieutenant, but owing to his age he was not called upon to serve abroad.

Burtles married Vera, daughter of C. E. Chalmers, Esq., of Wellington, Salop, in July, 1924, and leaves a son, born a few days after his death.

F. L. PYMAN.

REGINALD ARTHUR JOYNER.

BORN JANUARY 10TH, 1887; DIED OCTOBER 7TH, 1925.

DR. R. A. JOYNER lost his life as the result of an accident on Wednesday, October 7th, 1925, through an explosion in the research laboratories of Messrs. Nobel's Explosives Co., Ltd.

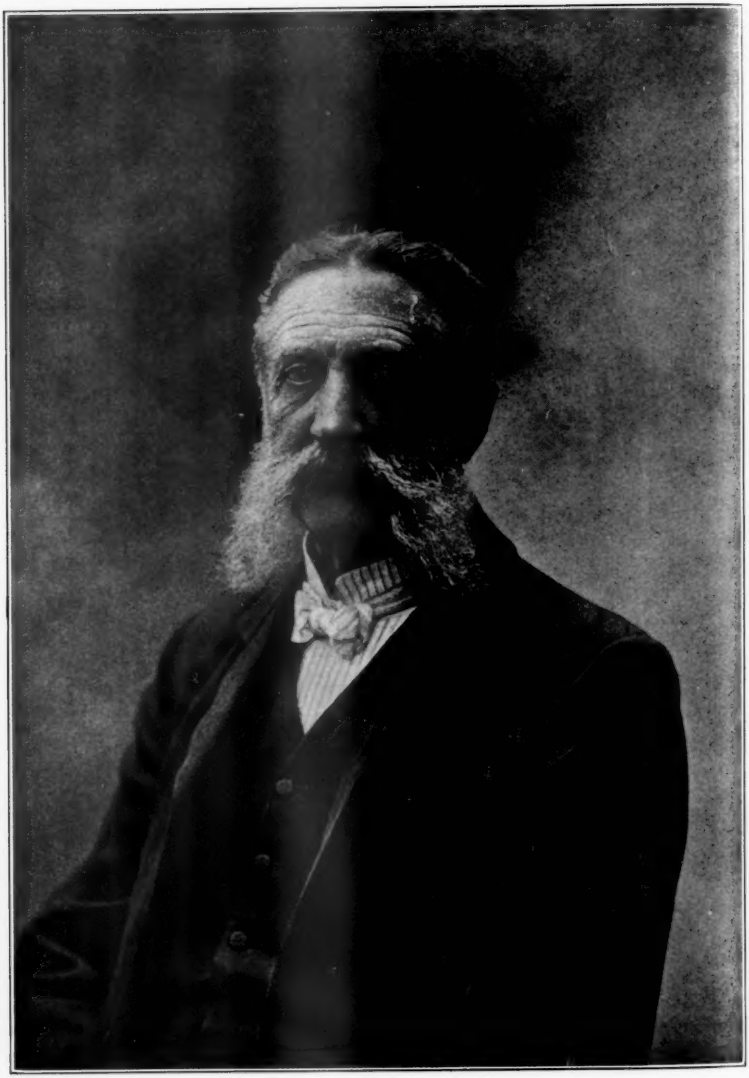
Dr. Joyner studied at University College, Bristol, taking a London degree with Honours in Chemistry in 1909, followed by the M.Sc. degree of the newly-founded University of Bristol in 1910. His work during this period is recorded in three papers on amalgams of silver and tin published in the *Journal* of the Chemical Society. These exhibit his careful and thorough experimentation and stand unaltered. They form the accepted basis of the treatment of dental amalgams in modern courses on Dental Metallurgy.

Joyner proceeded as an 1851 Exhibition Scholar to Zürich and afterwards followed Bredig to the Technische Hochschule, Karlsruhe, where he qualified for the degree of Doctor of Engineering, which has seldom been obtained by students from abroad. Bredig recognised his exceptional ability and independent judgment. Joyner published two very neat experimental papers; one dealt with the affinity constant of hydrogen peroxide; the other, on the catalysis of camphorcarboxylic acid by bases in various solvents, further elucidated the remarkable parallelism between ordinary reactions and life processes, showing a mechanism through which optical activity may play its well-known rôle.

For 12 years Dr. Joyner served on the Research Staff of Messrs. Nobel's at Ardeer. Most of the important work which he carried out on such war-time problems as mustard gas and explosives is, of course, not available for publication, but an estimate of his unusual experimental skill and scientific acumen may be obtained from a study of the paper which he published in the *Journal* of the Chemical Society on the "Viscosity of Solutions of Cuprammonium." His skill in the field of chemical technology is well illustrated by his patented process for the continuous manufacture of hydrazine (Brit. Pat. No. 199750 of 1923).

Those who came in contact with Joyner must have realised that few scientists showed such whole-hearted devotion and enthusiasm. He had many other interests, having been versatile in athletics and a keen territorial officer for many years. His straightforward and unassuming personality gained him, not only esteem, but also affection from all who knew him. In spite of the tragedy of his loss at the age of thirty-eight his widow and three children can look back with pride on his devoted work in the cause of science.

J. W. McB.



Guglielmo Körner

[To face p. 2975.]

GUGLIELMO * KÖRNER.

BORN APRIL 20TH, 1839; DIED MARCH 29TH, 1925.

GUGLIELMO KÖRNER was born in Cassel on April 20th, 1839. Having completed his course at the Polytechnic, he decided to devote himself to chemistry and studied under Will, Kopp, and Engelbach at Giessen, where he graduated in 1860. He remained at Giessen as assistant for 3 years and shortly after spent a year as student under Kekulé at Ghent. Early in 1865 he became assistant to Professor Odling at St. Bartholomew's Hospital; but at the end of the year returned to Ghent as private assistant and secretary to Kekulé, remaining there until the end of 1867, when the latter was elected to the chair of chemistry at Bonn.

At this time Kekulé was engaged in developing his theory of the aromatic compounds and in preparing his treatise on the same subject, and with this work Körner was closely associated. It is well known that Kekulé regarded his theory merely as a philosophic system which connected in a simple fashion the many isolated facts of aromatic chemistry and served as a useful means of explaining their relations; but he failed to grasp to the full extent its practical consequences. Körner, with a clearer and broader outlook, foresaw the possibility of establishing the theory on a sound experimental basis.

During his stay at Ghent Körner found time to carry out a number of researches, the most important of which were "the synthesis of resorcinol" and one entitled "Faits pour servir à la détermination du lieu chimique dans la série aromatique," published in 1867. In the preface to the former he points out that Kekulé's theory involves two problems not yet solved. He says, "Dans l'étude des cas d'isomerie dans les substances aromatiques on peut conséquemment se poser deux problèmes principaux: on peut d'abord chercher à établir par expérience quels sont les corps de même constitution, c'est-à-dire, dans lesquels la substitution se fait à des places correspondantes; on peut ensuite spécifier davantage ces places *en cherchant par combien d'atomes d'hydrogène elles sont séparées entre elles.* Dans sa plus grande généralité, ce dernier problème pourrait s'appeler la détermination du *lieu chimique* de l'atome substituant. . . . La solution du second problème paraît à première vue inaccessible à l'expérience. Je pense toutefois qu'on pourrait y parvenir." He embodies here the idea which

* Körner was christened Wilhelm and, strictly speaking, should bear that Christian name; but as he lived most of his life in Italy and never returned to his native land and was known by and published under the name Guglielmo, it seems right so to designate him.

underlay his life's work. In the same paper he brought forward a new fact in support of Kekulé's theory: for he succeeded in adding to the few di-derivatives, then known in three isomeric forms, a new and third iodophenol.

In the second paper, published in 1867, he gives an indication of the principle upon which his method of orientation is based. "Suppose," he says, "that the three dihydroxybenzenes give the same trihydroxybenzene, by the introduction of a third hydroxyl, it is obvious that the three hydroxyls must occupy the positions 1, 2, 4. In short, it is only this arrangement of the three hydroxyls which can combine in one compound the three dihydroxy-derivatives." It must be remembered that at this time methods of orientation were largely speculative.* It is true that by a fortunate act of intuition Baeyer assigned the correct constitution to mesitylene and Graebe gave the true formula to phthalic acid; but, on the other hand, some of the suggestions were less happy. Quinol, for reasons into which we need not enter, was assumed to be an ortho-compound, salicylic acid a meta-compound, and ordinary dinitrobenzene a para-compound, and so forth, assumptions which subsequently led to ever increasing confusion as relationships became more clearly and closely established.

For reasons of health Körner left Ghent for Palermo in 1867 and entered the laboratory of Cannizzaro, where he continued to work indefatigably, collecting fresh experimental facts connected with the problem which he had set out to solve. In the two years which followed, this material had so far accumulated that Cannizzaro induced Körner to publish it, although the latter would have preferred to withhold it until it had reached a more complete form.

This memoir, which involved a stupendous amount of brilliant experimental work, appeared in 1869 in the *Giornale di Scienze Naturali ed Economiche* of Palermo under the title "Facts which serve for the determination of the chemical position in aromatic compounds." After a short introduction by Cannizzaro, the memoir begins with a clear account of Kekulé's theory on the constitution of benzene and the kinds of isomerism to which it gives rise. Körner shows that the non-existence of more than one monoderivative and the special kind of isomerism existing among the polysubstituents of benzene is based on the hypothesis of the equivalence of the six valencies of the carbon atoms of the

* An excellent account of the development of the views on orientation is given in Roscoe and Schorlemmer's "Treatise," vol. iii, part iii (Introduction) and also in the introduction by Richard Meyer to Erlenmeyer's "Lehrbuch der organischen Chemie," vol. ii (Leipzig, 1882).

nucleus and the relative positions occupied by two or more substituent elements or groups. He then proceeds to bring experimental evidence of the equivalence of the six atoms of hydrogen. Beginning with the three hydroxybenzoic acids, he shows that by eliminating carbon dioxide the same phenol results. Thus, the differences in the three acids must be due to the relative positions of the groups. By substituting chlorine for hydroxyl and replacing the halogen by hydrogen with the aid of sodium amalgam, he obtained the same benzoic acid in all three cases. These experimental facts, due partly to Körner and partly to Graebe and Beilstein, demonstrate completely the equivalence of three positions in the nucleus.

A fourth position was determined as follows: the nitroaniline (para) of Arppe can be transformed into chlorobromobenzene in two ways, either by substituting chlorine for the amino-group and bromine for the nitro-group or *vice versa*, and the same product results. As this nitroaniline can be proved to belong to the same series as one of the hydroxybenzoic acids, it follows that the position occupied by the phenol residue in the three acids is equivalent to that in a fourth position corresponding to the amino- or nitro-group in nitroaniline. The fifth and sixth positions were attacked in a similar fashion.

One of the nitrophenols belongs to the same series as salicylic acid. A bromine atom and an additional nitro-group can be introduced into this nitrophenol, with the result that the product is identical with that obtained by substituting two nitro-groups for two atoms of hydrogen in bromophenol and thus bromonitro-*nitrophenol*, $C_6H_2 \cdot NO_2 \cdot Br \cdot OH \cdot NO_2$, is identical with dinitro-*bromophenol*, $C_6H_2 \cdot NO_2 \cdot NO_2 \cdot OH \cdot Br$, which signifies that in nitrophenol there are two positions of equal value and symmetrical one with the other in respect of the hydroxyl. There are therefore five equivalent positions. Granted the existence of two symmetrical positions and imagining a plane drawn at right angles through the centre of these two positions, the molecule will be divided into two symmetrical halves, which implies the existence of a second symmetrical pair and it may be therefore concluded that the six positions occupied by hydrogen in the molecule of benzene are of equal value.

Unfortunately, the publication in which this paper appeared was little known to the chemical world, and it was only later that its full significance was realised and its conclusions accepted. Meanwhile, as already stated, the confusion which reigned on the subject of orientation continued to grow.

Whilst at Palermo Körner sent a paper to the Academie des

Sciences on the "Synthesis of a base isomeric with Toluidine," which he obtained by nitrating and reducing *p*-bromotoluene. The paper is interesting from the fact that in it he proposes the formula for pyridine, which is now adopted. His reference to this formula was, however, suppressed in the paper sent to the Academie, probably from its purely theoretical nature, but was afterwards published (1869) as a note in the *Giornale di Scienze Naturali ed Economiche.*

We will leave for a moment Körner's experimental work in order to take up the thread of his subsequent career.

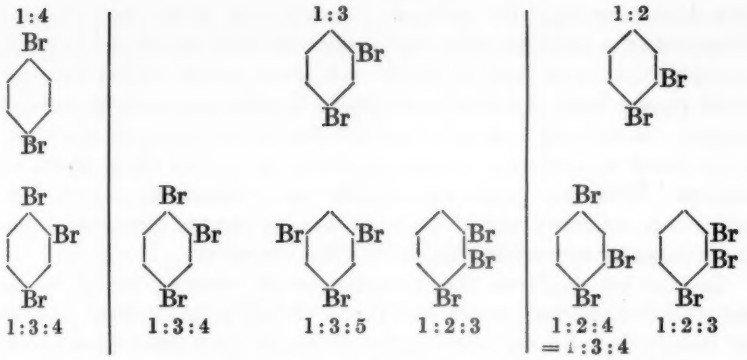
In 1870 the "Scuola Superiore di Agricoltura" was founded at Milan and Körner was elected to the chair of organic chemistry, where he continued with his usual energy to prosecute his experimental studies. In 1874 his classical memoir on "Studi sull' Isomeria delle cose dette Sostanze Aromaticee a shi atomi di carbonio" appeared in the *Gazzetta Chimica Italiana,* in which is collected a mass of new material, the preparation of which had occupied him during the preceding five years.

He begins by explaining the weak points in the views of previous observers on orientation and shows that the only satisfactory method is the one outlined in his paper of 1867.

"For more than six years," he says, "a number of distinguished chemists have occupied themselves with the study of isomerism of the so-called aromatic compounds and still continue to do so. Nevertheless it is a curious fact that no definite solution has up to the present been reached." Further he says: "The most certain method I still believe to be the one suggested seven years ago in my first work on this subject, namely, the transformation of the three isomeric di-derivatives into the isomeric tri-derivatives."

He suggests then the utilisation of the three dibromobenzenes as affording the fewest experimental difficulties.

"The equivalence of the six positions of hydrogen in benzene being granted, it suffices to prepare any complete series of trisubstituted derivatives with these three compounds and to study their relation and in this way an unequivocal solution of the problem will be attained. Thus, by preparing the three possible tribromobenzenes from the dibromobenzenes and discovering for each one of them how many and which of the tribromobenzenes can be prepared or, *vice versa,* finding from the latter to which of the dibromobenzenes it gives rise, a direct and definite method will be afforded for determining the structure of both the di- and tribromobenzenes according to the following scheme:



In the same way, it is possible to prepare the six modifications of dibromoaniline and also the six nitrodibromobenzenes."

The principle, as we know, is simple, elegant, and beyond criticism and has never been seriously questioned.

We have only to survey the number and variety of new compounds, new reactions and new and ingenious devices for obtaining the same substance by different methods, to realise the amount of patient and careful work and experimental skill which this truly classical research entailed.

As his fellow-worker and biographer, Professor Menozzi, has said, "the work suffices to raise Körner to a distinguished position among the great chemists."

In addition to devising a method of orientation independent of any speculation, Körner was able to lay down certain rules of substitution, which possess, not only a scientific interest, but one of great practical value. Putting it very briefly, he showed that if the halogens or nitric acid act on the halogen derivatives of benzene or on aniline, phenol, or toluene so that one atom of hydrogen is substituted, the principal product is the 1 : 4-derivative and, as a secondary product, the 1 : 2-derivative, and the more violent the reaction the larger the quantity of the latter. Where the original group is CO_2H, NO_2, or SO_3H, the principal derivative is a 1 : 3-compound and at the same time a certain amount of 1 : 2- and occasionally 1 : 4-derivative is produced.

If sulphuric acid is allowed to act on the members of the above series, the product is mainly the 1 : 3-derivative with smaller and variable quantities of the 1 : 2-derivative.

At the end of the paper Körner discusses Kekulé's formula for benzene with the alternate double linkages. He shows that the simultaneous formation of 1 : 2- and 1 : 4-derivatives in certain cases and of 1 : 3-derivatives in others cannot be explained by

Kekulé's formula. He proposes one which had already been indicated in a former paper and resembles that of Claus inasmuch as each atom of carbon is linked with three others. This arrangement presupposes the twelve atoms to be disposed in four parallel planes; in each of the outer planes are three atoms of hydrogen 1, 3, 5 and 2, 4, 6 and in each of the inner planes three atoms of carbon. This arrangement affords the maximum symmetry, represents absolute equivalence of the hydrogen atoms and the three cases of isomerism among the di-derivatives.

Besides his work on the constitution of benzene, to which he devoted the greater part of his time and thought, his deep interest in botany led him to the study of many vegetable substances. Between the years 1875 and 1895 he published a series of papers dealing with products of the vegetable kingdom such as the constitution of veratric acid and veratrole, the conversion of aspartic into fumaric acid, on two acids isomeric with vanillic acid, on caffeic acid from cinchona cuprein, on the alkaloids of angustura bark, the constitution of siringina and, in collaboration with Menozzi, on the transformation and synthesis of amino-acids. By the action of methyl iodide on amino-acids in presence of alkali, ammonia is eliminated and an unsaturated acid results: thus aspartic acid gives fumaric acid, alanine is converted into acrylic acid, and leucine into an unsaturated acid containing six carbon atoms. The reverse process was also investigated and carried to a successful issue.

Of Körner's personal character, Professor Angelo Menozzi, a former student and collaborator, has given his impressions in a memorial address, from which the following abstracts have been taken.*

The first thing that strikes one, he says, is that Professor Körner possessed in an eminent degree that quality of the true scientist who devotes himself to the study of science for its own sake, independently of any practical application his discoveries may be found to possess. It so happened that Körner's discoveries, though of scientific importance of the first order, have brought in their train practical results of great value. Körner belongs to that group of scientists who affirm nothing without a rigorous and complete proof and are never in a hurry to publish results. This quality he possessed in an excessive degree. It is certain that it took some pressure on the part of Cannizzaro to persuade Körner to publish his first paper on orientation. Furthermore, the con-

* I wish here to express my indebtedness to my friend Prof. Nasini for the many documents relating to Körner which he was good enough to place at my disposal and also for the photograph which is reproduced here.

stitution of orcin had been established in Körner's laboratory before Tiemann's research appeared in the *Berichte*. The same is true of leucine, the constitution of which was fully known before its publication elsewhere. He recognised this weakness in himself, but as it was of secondary importance to his work, he put it aside as a matter of small significance. Whilst one cannot but regret this excessive caution which led him to control with scrupulous care every conclusion and statement before publication and which may have robbed him of priority in certain discoveries, one cannot but admire a quality which is only too rare among scientific workers of the present day. Körner possessed a keen intuition, which was soon recognised by those with whom he worked. He declared the acid isolated from aspartic acid to be fumaric acid long before its identity was definitely established and the same thing occurred with caffeic acid from angustura.

As a teacher Körner was lucid, profound and effective and his lectures left a lasting impression on the many students who attended his classes.

His method was largely based on experimental demonstrations and Cannizzaro relates that when acting as lecture assistant his arrangement of the experiments was a model of precision and ingenuity. He was skilled in analysis by the dry way and insisted on his students becoming proficient in this method. In the execution of his own researches, in his skill as an experimenter, in the originality of his ideas and in the novelty of his methods he showed a master mind.

He had a passion for preparing his specimens in a state of extreme purity and it is this personal characteristic which is responsible for that remarkable collection of organic substances which is one of the scientific treasures of the School of Agriculture of Milan and is unique in the variety, purity, and beauty of the preparations.

Körner's system of imparting information was essentially practical, for he never forgot that he was teaching in a school of agriculture. If a substance was connected with plant life—he was a passionate lover of flowers and plants and possessed a profound knowledge of plant physiology—he never failed to enlarge upon this relation; similarly any reference to an industrial commodity led to an account of its technical application.

He completed his 75th year in 1914, when, according to the existing rule, he reached the retiring age; but at the instance of the staff of the agricultural school, supported by the Chemical Society of Milan, his services were exceptionally retained until 1922, when for reasons of failing health he resigned his chair at the advanced age of 83.

He lived his last three years in peaceful retirement, happy in his family life and in the visits of his former colleagues and pupils, and passed quietly away on the evening of March 29th, 1925.

Körner was elected honorary member of many Italian and foreign institutions, *viz.*, the Reale Accademia dei Lincei, the Reale Istituto Lombardo di Scienze e Lettere, La Società Italiana delle Scienze, received the honorary doctorate of Oxford, Cambridge, and Giessen, was awarded the Davy medal of the Royal Society and made honorary member of the Royal Institution, of the Chemical Society of London, and of the German Chemical Society. He was enrolled chevalier of the civil order of Savoy for work of scientific merit.

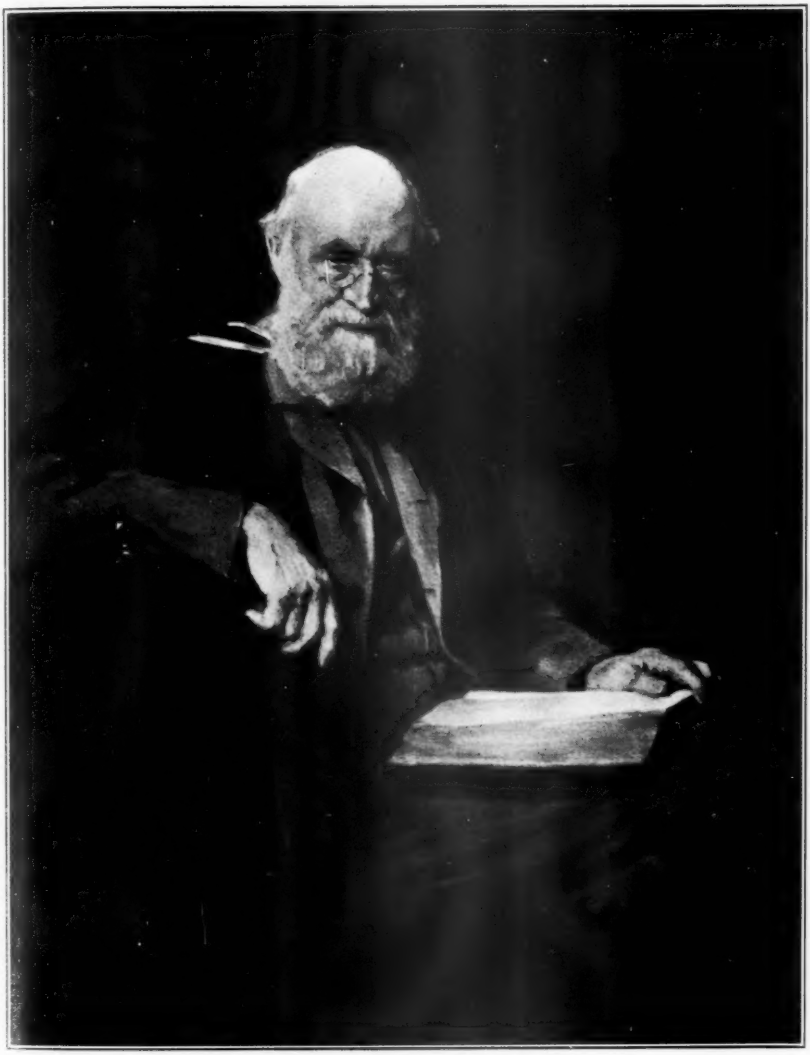
J. B. COHEN.

GEORGE DOWNING LIVEING.

BORN DECEMBER 21ST, 1827; DIED DECEMBER 26TH, 1924.

BY the death of Dr. G. D. Liveing, Professor of Chemistry in the University of Cambridge, at the great age of ninety-seven, the Society loses its oldest member, as he was elected Fellow in 1853. He was the son of Edward Liveing of Nayland, Suffolk. Entering at St. John's College, Cambridge, he was eleventh wrangler in 1850, and, in the following year, he took the Natural Sciences Tripos, then instituted for the first time, and obtained a first class with distinction in Chemistry and Mineralogy. After working in Berlin with Rammelsberg, he was elected to a fellowship at St. John's College in 1853, but, under the Statutes of that period, he had to resign on his marriage in 1860. After acting as Deputy to the Professor of Chemistry (Reverend J. Cumming), he was elected to the Chair in 1861.

It is difficult to convey an idea of the attitude of the University at this period towards the experimental sciences, steeped as it was in the tradition of centuries of classical, mathematical and theological teaching. There was no laboratory instruction for students, although some experiments seem to have been shown in the lectures. Liveing relates how, in 1850, he was attending Mr. Griffin's lectures on Physical Optics and, whilst dealing with the subject of the Fraunhofer lines, the lecturer asked any who wished, to come again later and he would demonstrate their formation. Liveing was the only one in the class who accepted the offer. The apparatus consisted of Wollaston's arrangement for producing a pure spectrum. A prism, a lens, a slit illuminated by an oil lamp, and a screen. Between the lamp and the slit was placed a bottle con-



Sincerely yours

G. D. Livermore

[*To face p.* 2982.]

taining some copper turnings on which nitric acid was poured. A series of fine black lines appeared on the screen. The explanation of the formation of the black lines was not given by Bungen and Kirchoff until 1860. Liveing had to fight a long and hard battle to persuade the University that it was their duty to teach the experimental sciences, not by merely showing experiments on a lecture table, but by the only sure method, of making the students perform them themselves.

St. John's College, soon after Liveing took his degree, built him a chemical laboratory and "sowed the first seed towards the growth of a large chemical school," and they allowed him to use this laboratory after he became Professor of Chemistry. The question of providing teaching in experimental sciences had still to be fought out. Plans were drawn up, but when the tenders came in they far exceeded the money the University had to spend. The laboratory proposed for Chemistry, by Professor Willis, consisted of "a building which was capable of standing violent explosions and as uninflammable as possible, containing a series of vaults." Liveing would have none of this, and begged that Chemistry should be left out of the scheme. The result of his action was that Chemistry was only housed in a temporary structure for many years until, in 1887, a laboratory was built on the Pembroke Street site. This building was added to in 1908 and again in 1920, and the department of Physical Chemistry has also taken over the large laboratory vacated by the Engineering department. Altogether the laboratory has accommodation for more than 700 research and ordinary students and is the largest chemical laboratory in the country.

Liveing's contributions to science were on the transmutation of the elements in 1855, and a few papers on geological and chemical subjects. In 1875, Sir James Dewar was appointed Jacksonian Professor of Chemistry, and the two professors almost at once began their researches on the spectroscope, which continued until 1904. These papers have been collected in one large volume and published by the University Press (1915). The work was characterised by its great accuracy, originality, and the patience with which one difficulty after another was overcome, and is now regarded as one of the standard books on the subject.

As a lecturer, Liveing was inspiring to those who had sufficient mathematical ability to follow him. The lectures were illustrated by experiments carefully chosen, and invariably rehearsed, but the experiments not unfrequently failed from his over-anxiety to make them succeed. As the head of a large department, he maintained a stern discipline, and to the younger men he appeared somewhat

unapproachable. Those who knew him intimately, however, were aware that he was the kindest and most liberal of men, and a delightful companion, especially when he was in the mood to tell stories of byegone Cambridge and of his travels, during which he collected specimens of minerals to illustrate his lectures.

Liveing, in addition to his professorial duties, found time to attend with great regularity the magisterial bench and many philanthropic and benevolent committees. For several years he held a commission as captain in the Town and County Rifle Corps; he was also an enthusiastic gardener.

It is not generally known that for the last four years of his life he was actively engaged in an experimental investigation on the absorption of radiant energy by dense substances such as barium sulphate, lead sulphate, cassiterite, litharge, etc. Each vacation he devoted an hour or two every day to working at these problems in the Goldsmiths' metallurgical laboratory, and he spent much time at home in working out his results. This research is far from complete, although it is an amazing testimony to his vigour and perseverance. It was whilst on his way to the laboratory that he met with the accident which caused his death a few weeks later. Liveing resigned his professorship in 1908 and was given the degree of Sc.D.

C. T. Heycock.

ALEXANDER MITCHELL WILLIAMS.

Born September 20th, 1888; Died February 21st, 1925.

The son of a master-baker, Alexander Mitchell Williams was born on September 20th, 1888, at Burntisland in Fifeshire. He attended Burntisland School and later George Watson's College in Edinburgh, where at the age of seventeen he was dux and gold medallist. With the John Welsh mathematical bursary (a foundation of Thomas Carlyle in memory of his father-in-law), Williams entered the University of Edinburgh and had a brilliant record in Mathematics, Physics, and Chemistry. In 1910 he graduated as B.Sc. and as M.A. with first-class honours in Mathematics and Natural Philosophy. During his University period, he gained many scholarships and prizes, being awarded finally an 1851 Exhibition Scholarship which enabled him to proceed to Sweden and work under the guidance of Arrhenius. His chief study in Stockholm was adsorption, a subject which occupied his attention for many years afterwards. On returning to this country he continued research work in the laboratories of Professor Donnan in Liverpool

and in London. In 1915 he was appointed science teacher in Hawick High School, and while there had a serious breakdown in health, from which he never entirely recovered. After temporary service in the Science Department of his old school in Edinburgh, he became a lecturer in the Chemistry Department of Edinburgh University in 1916. Continuing his research work, he graduated as D.Sc. with a thesis on Adsorption. In 1919 he was appointed joint Head of the Physico-chemical Department at the Shirley Institute, Didsbury, the headquarters of the Cotton Industry Research Association. Soon after his appointment he married Miss May Shaw, an Edinburgh lady.

While in Edinburgh, Williams published four valuable papers on adsorption ("Thermodynamics of Adsorption," *Proc. Roy. Soc. Edin.*, 1918, **38**, 23; "The Adsorption Isotherm at Low Concentrations," *ibid.*, p. 48; "The Adsorption of Gases at Low and Moderate Concentrations," Parts I and II, *Proc. Roy. Soc.*, 1919, **96**, *A*, 287; Part III, *ibid.*, p. 298), together with one on "Periodic Precipitation," jointly with Miss M. R. Mackenzie (J., 1920, **117**, 844), and a paper on the "Depolarisation by Oxygen of a Voltaic Cell" (*J. Soc. Chem. Ind.*, 1920, **39**, 285T).

The work of Williams at the Shirley Institute was chiefly concerned with the moisture relations of cotton, and the swelling of cotton cellulose under the influence of alkalis. The results of his researches are published in the *Journal* of the Textile Institute. He showed that the swelling in mercerisation cannot be simply referred to the concentration of the hydroxide ion in the alkali solutions, but is dependent to some extent on a specific effect of the alkali metal. The work so far published may be regarded as a considerable instalment of a systematic account of the nature and reactions of the cotton gel—an account which, when complete, should give to those who use cotton in the textile arts increased powers in manipulating their material. One positive technical success Williams achieved by his discovery of a method for preparing cotton yarn of high insulating power, so making it possible for English firms to compete in a trade which had long been a continental monopoly.

Williams had a first-rate scientific intellect, both critical and constructive. He was a sympathetic and kindly teacher, and his investigations, like all that he did, were carried out with an energy and a fervour of enthusiasm which the state of his bodily health could ill support. A final attack of his insidious malady at the end of 1924 led to his untimely death on February 21st, 1925.

J. W.

GEORGE YOUNG.

BORN SEPTEMBER 9TH, 1867; DIED APRIL 3RD, 1925.

GEORGE YOUNG, the younger son of Archibald Young, surgical instrument maker, was born in Edinburgh on September 9th, 1867. He was educated in Edinburgh at the Collegiate School, George Watson's College, and Minto House. He pursued the study of chemistry at the Polytechnik, Munich, and graduated in 1891 at the University of Erlangen. Soon after returning home, he was appointed demonstrator of chemistry at Firth College, Sheffield, and was afterwards promoted to the lectureship in organic chemistry, a post which he filled with eminent success. Young was an excellent teacher and was most successful in interesting students in research. He contributed many papers on organic chemistry to this *Journal* between the years 1895 and 1905, dealing with the constitution of amidines, the action of ammonias on acetyl urethane, triazoles and their derivatives, and kindred subjects. He was a Fellow of the Chemical Society, of the Institute of Chemistry, and a member of the Society of Chemical Industry.

In his school days, Young was well known in athletic circles as a good sprinter. At Firth College he took a lively interest in the life of the College; he started a students' Chemical Society and at the outbreak of the Boer war he played a vigorous part in organising a company of students, which was attached to the West Yorkshire Royal Engineers. He served with marked success as sergeant-major to the company.

Young severed his connection with the College in 1904, owing to ill health, and moved to London in 1906, where he established a consulting practice. During the Great War he directed his energies to industrial problems with a view to the production of chemicals formerly imported from Germany.

Dr. Young died on April 3rd, 1925, leaving a wife and three daughters to mourn his loss.

W. C. W.

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Veratrylideneaminoacetal (FORSYTH, KELLY, and PYMAN), 1665.
1-Veratryl-6:7-methylenedioxydihydro-*iso*quinoline methiodide (HAWORTH, PERKIN, and RANKIN), 2020.
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β-Veratrylpropionic acid, α-cyano-, (BAKER and ROBINSON), 1433.
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Violuric acid, absorption spectra and ionisation of (MORTON and TIPPING), 2514.
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FORMULA INDEX.

THE following index of organic compounds of known empirical formula is arranged according to Richter's system (see *Lexikon der Kohlenstoff-Verbindungen*).

The elements are given in the order C, H, O, N, Cl, Br, I, F, S, P, and the remainder alphabetically.

The compounds are arranged—

Firstly, in groups according to the number of carbon atoms (thus C_1 group, C_2 group, etc.).

Secondly, according to the number of other elements besides carbon contained in the molecule (thus 5 IV indicates that the molecule contains five carbon atoms and four other elements).

Thirdly, according to the nature of the elements present in the molecule (given in the above order).

Fourthly, according to the number of atoms of each single element (except carbon) present in the molecule.

Salts are placed with the compounds from which they are derived. The chlorides, bromides, iodides, and cyanides of quaternary ammonium bases, however, are registered as group-substances.

C_1 Group.

CH_4 Methane, ignition of mixtures of air with (WHEELER), 14.

CCl_4 Carbon tetrachloride, dielectric constant of (HARRIS), 1065.

1 II

$CHCl_3$ Chloroform, dielectric constant of (HARRIS), 1066.

CH_2O Formaldehyde, vapour pressure of, in aqueous solutions (BLAIR and LEDBURY), 26, 2832.

CH_2O_2 Formic acid, velocity of reaction of bromine with (HAMMICK, HUTCHISON, and SNELL), 2715; action of, on sesquiterpenes (ROBERTSON, KERR, and HENDERSON), 1944.

CH_2Te_2 Ditelluromethane (MORGAN and DREW), 537.

CH_4O Methyl alcohol, preparation of pure (HARTLEY and RAIKES), 524.

CH_5N Methylamine, detection of, in presence of ammonia (VALTON), 40.

CNS Thiocyanogen, action of, on unsaturated compounds (CHALLENGER and BOTT), 1038.

1 III

$CH_2Cl_6Te_2$ Methylenebistelluritrichloride (MORGAN and DREW), 536.

CH_4ON_2 Carbamide, reaction of sodium hypobromite with (DONALD), 2255.

1 V

CHO_3ClBrS Chlorobromomethanesulphonic acid, optical activity of, and its salts (READ and MCMATH), 1572.

C_2 Group.

C_2H_2 Acetylene, explosion of mixtures of nitrogen and (GARNER and SAUNDERS), 77.

2 II

$C_2H_2O_4$ Oxalic acid, formation of, from ether, and its uranium salts (ROWELL and RUSSELL), 2900; dissociation constants of (BRITTON), 1905; tervalent molybdenum salts (WARDLAW and PARKER), 1311; silver salt, decomposition of (MACDONALD and HINSHELWOOD), 2764.

$C_2H_4Cl_2$ Ethylene dichloride, dielectric constant of (HARRIS), 1066.

C_2H_6O Ethyl alcohol, partial pressures of aqueous solutions of (Dobson), 2866; swelling and dispersion of colloids in mixtures of ether and (Mardles), 2940; catalysis by alumina of the reaction between ammonia and (Dorrell), 2399.

2 III

$C_2HO_2Cl_3$ Trichloroacetic acid, additive compounds of, with esters (Kendall and Booge), 1771.

$C_2H_4OCl_2$ *s*-Dichlorodimethyl ether, condensation of phenylethylamine with (Short), 269.

2 IV

$C_2H_3O_5ClS$ Chlorosulphoacetic acid, preparation and resolution of, and its salts (Backer and Burgers), 233.

$C_2H_5O_2SNa$ Sodium ethyl sulphoxylate (Vogel and Partington), 1522.

C_3 Group.

$C_3H_4O_4$ Malonic acid, dissociation constants of (Britton), 1906; alkaline earth salts, solubilities of (Walker), 62.

$C_3H_6O_2$ Methyl acetate, equilibrium of the hydrolysis of (Burrows), 2723.

$C_3H_6O_3$ Trioxymethylene, action of, on Grignard reagents (Marshall), 2188.

$C_3H_8O_3$ Glycerol, ionic activity of water in aqueous solutions of (Colvin), 2788; liquid and vapour phases of aqueous mixtures of (Iyer and Usher), 841.

3 IV

$C_3H_{10}Cl_3SbPd$ Trimethylstibinedichloropalladium hydrochloride (Morgan and Yarsley), 190.

C_4 Group.

$C_4H_4O_2$ Methyl propiolate (Ingold), 1203.

$C_4H_4O_4$ Fumaric acid, Röntgen ray structure of (Yardley), 2207; thallous salt (Christie and Menzies), 2370.

Maleic acid, Röntgen ray structure of (Yardley), 2207; thallous salt (Christie and Menzies), 2370.

C_4H_6O Acetic anhydride, interaction of tellurium tetrachloride and (Morgan and Drew), 531.

$C_4H_6O_4$ Succinic acid, dissociation constants of (Britton), 1906; alkaline earth salts, solubilities of (Walker), 62; thallous salt (Christie and Menzies), 2370.

$C_4H_6O_6$ Tartaric acid, dissociation constants of (Britton), 1905; thallous salt (Christie and Menzies), 2371.

$C_4H_7N_3$ 2-Amino-4(5)-methylglyoxaline (Burtles and Pyman), 2017.

C_4H_8O Methylvinylcarbinol, resolution and rotation of (Kenyon and Snellgrove), 1174.

$C_4H_8O_2$ Ethyl acetate, effect of salts, sugars, and temperature on solubility of (Glasstone and Pound), 2660.

$C_4H_8S_2$ Triethylene trisulphide, supposed true nature of (Bennett and Berry), 910.

$C_4H_{10}O_2$ Ethyl ether, swelling and dispersion of colloids in mixtures of alcohol and (Mardles), 2940; oxidation of, to oxalic acid in presence of uranyl nitrate (Rowell and Russell), 2900.

$C_4H_{10}O_3$ α-Methyl glycerol (Gilchrist and Purves), 2744.

4 III

$C_4H_3O_4N_3$ Violuric acid, absorption spectra and ionisation of (Morton and Tipping), 2514.

$C_4H_6O_4Te$ Tellurodiacetic acid, and its salts (MORGAN and DREW), 535.
$C_4H_6O_4Te_2$ Ditellurodiacetic acid (MORGAN and DREW), 536.
$C_4H_8OCl_2$ β-Methyl αγ-dichlorohydrin (GILCHRIST and PURVES), 2743.
$C_4H_8Cl_2Se$ ββ′-Dichlorodiethyl selenide (BELL and GIBSON), 1882.
$C_4H_8Cl_4Se$ ββ′-Dichlorodiethyl selenide dichloride (BELL and GIBSON), 1880.
$C_4H_8Br_2Se$ ββ′-Dibromodiethyl selenide (BELL and GIBSON), 1883.
$C_4H_8Br_4Se$ ββ′-Dibromodiethyl selenide dibromide (BELL and GIBSON), 1881.
$C_4H_{11}O_2P$ Diethylphosphinic acid, silver salt of (COLLIE), 964.

4 IV

$C_4H_5O_2N_3S$ Nitrothiol-2-methylglyoxaline, and its ammonium salt (BHAGWAT and PYMAN), 1835.
$C_4H_5O_4NCl_2$ Ethyl dichloronitroacetate (MACBETH and TRAILL), 895.
$C_4H_5O_4NBr_2$ Ethyl dibromonitroacetate (MACBETH and TRAILL), 896.
$C_4H_6O_4Cl_2Te$ Dichlorotelluridiacetic acid (MORGAN and DREW), 534.
$C_4H_7OCl_3Te$ Tellurium methylethylketone trichloride (MORGAN and ELVINS), 2628.
$C_4H_8Cl_2Br_2Se$ ββ′-Dibromodiethyl selenide dichloride (BELL and GIBSON), 1883. ββ′-Dichlorodiethyl selenide dibromide (BELL and GIBSON), 1883.
$C_4H_9O_4N_2Cl$ Ammonio-derivative of ethyl chloronitroacetate (MACBETH and TRAILL), 895, 1122.
$C_4H_9O_4N_2Br$ Ammonio-derivative of ethyl bromonitroacetate (MACBETH and TRAILL), 896.
C_4H_9ClSHg *iso*Butyl mercaptan mercurichloride (BIRCH and NORRIS), 905.
$C_4H_{10}O_4N_2Cl$ Ethyl chloronitroacetate hydrazide (MACBETH and TRAILL), 1122.
$C_4H_{10}Cl_2S_2Cd$ Dimethyldithiolethylene cadmium chloride (MORGAN, CARTER, and HARRISON), 1922.
$C_4H_{10}Cl_2S_2Zn$ Dimethyldithiolethylene zinc chloride (MORGAN, CARTER, and HARRISON), 1921.
$C_4H_{10}Br_2S_2Cd$ Dimethyldithiolethylene cadmium bromide (MORGAN, CARTER, and HARRISON), 1922.
$C_4H_{10}I_2S_2Zn$ Dimethyldithiolethylene zinc iodide (MORGAN, CARTER, and HARRISON), 1921.

4 V

$C_4H_5O_4NClBr$ Ethyl chlorobromonitroacetate (MACBETH and TRAILL), 896.

C_5 Group.

C_5H_5N Pyridine, distribution of, between water and benzene (WOODMAN and CORBET), 2461.
$C_5H_8N_2$ 2-Amino-4:5-dimethylglyoxaline, and its salts (BURTLES and PYMAN), 2015.
$C_5H_{10}O$ Ethylvinylcarbinol, resolution and rotation of (KENYON and SNELLGROVE), 1175.
$C_5H_{10}O_5$ Arabinose, constitution of (HIRST and ROBERTSON), 358.
$C_5H_{10}S$ Pentamethylene sulphide, and its salts (THIERRY), 2758.
$C_5H_{12}O_3$ αβ-Dimethylglycerol (GILCHRIST and PURVES), 2743.

5 III

$C_5H_3O_5N_3$ 3:5-Dinitro-4-pyridone (CROWE), 2029.
$C_5H_4O_3N_2$ 3-Nitro-4-pyridone (CROWE), 2028.
$C_5H_5O_3N_3$ 3-Nitro-5-amino-4-pyridone, and its hydrochloride (CROWE), 2029.
$C_5H_5O_4I$ 1-Iodo*cyclo*propane-1:2-dicarboxylic acid (ING and PERKIN), 2394.
$C_5H_6ON_2$ 3-Amino-4-pyridone, and its salts (CROWE), 2029.

$C_5H_7O_2N_3$ Nitro-1:2-dimethylglyoxalines, and their salts (BHAGWAT and PYMAN), 1833.

$C_5H_7O_4K$ Potassium ethyl malonate, electrolysis of (ROBERTSON), 2057.

$C_5H_8N_2S$ 2-Methylamino-4-methylthiazole, and its hydrochloride (BURTLES, PYMAN, and ROYLANCE), 588.

2-Thioldimethylglyoxalines (BURTLES, PYMAN, and ROYLANCE), 586.

$C_5H_{10}O_2N_2$ Glutardialdoxime, preparation of (SHAW), 215.

Malonmonoethylamide (WEST), 750.

$C_5H_{11}IS$ Tetramethylene sulphide methiodide (THIERRY), 2758.

$C_5H_{12}O_4N_2$ Hydrazine derivative of ethyl α-nitropropionate (MACBETH and TRAILL), 897.

5 IV

$C_5H_8O_4NCl$ Ethyl α-chloronitropropionate (MACBETH and TRAILL), 896.

$C_5H_8O_4NBr$ Ethyl α-bromonitropropionate (MACBETH and TRAILL), 897.

$C_5H_9OCl_3Te$ Tellurium diethylketone trichloride (MORGAN and ELVINS), 2629.

$C_5H_9O_3N_2Br$ Bromomalonmonoethylamide (WEST), 751.

C_6 Group.

C_6H_6 Benzene, dielectric constant of (HARRIS), 1065; cryoscopy with (JONES and BURY), 1947.

6 II

$C_6H_4O_2$ *p*-Benzoquinone, preparation of (CRAVEN and DUNCAN), 1489.

$C_6H_4O_6$ 3:5-Dinitrocatechol, colorimetric dissociation constants of (LAXTON, PRIDEAUX, and RADFORD), 2499.

4:6-Dinitroresorcinol, colorimetric dissociation constants of (LAXTON, PRIDEAUX, and RADFORD), 2499.

C_6H_6O Phenol, surface tension of aqueous solutions of (GOARD and RIDEAL), 780, 1668; molecular condition of, in benzene (PHILIP and CLARK), 1274; effect of salts on the equilibrium and critical solution temperature of, in water (CARRINGTON, HICKSON, and PATTERSON), 2544; equilibrium of salicylic acid, water, and (BAILEY), 1951.

$C_6H_6O_3$ *cis*-1-Methyl*cyclo*propane-1-2-dicarboxylactone (INGOLD), 398.

Phloroglucinol, absorption spectra of (MORTON and ROGERS), 2700.

$C_6H_6O_4$ Phthalic acid, thallous salt (CHRISTIE and MENZIES), 2370.

C_6H_7N Aniline, physical properties of, and its aqueous solutions (APPLEBEY and DAVIES), 1836.

$C_6H_8O_4$ αγ-Dialdehydopropane-β-carboxylic acid (PERKIN and PINK), 194.

Hydroxy-α-methylglutarolactones, and their salts (INGOLD), 394.

cis- and *trans*-1-Methyl*cyclo*propane-1:2-dicarboxylic acids, and their salts (INGOLD), 396.

$C_6H_{10}O_2$ Ethyl acetoacetate, interaction of *o*-hydroxydistyryl ketones and (HEILBRON, FORSTER, and WHITWORTH), 2159.

$C_6H_{10}O_5$ Dextrin, constitution of (IRVINE and OLDHAM), 2914.

Hydroxy-α-methylglutaric acids, and their salts (INGOLD), 394.

Methylitamalic acid, barium salt (INGOLD), 397.

$C_6H_{12}O$ *n*-Propylvinylcarbinol, resolution and rotation of (KENYON and SNELLGROVE), 1176.

$C_6H_{12}O_6$ Dextrose, dissociation constant of (BRITTON), 1902.

$C_6H_{12}S_2$ Hexamethylene disulphide (BENNETT and HOCK), 2676.

$C_6H_{14}O_3$ Trimethyl glycerol (GILCHRIST and PURVES), 2744.

$C_6H_{14}S$ *iso*Propylmercaptan *n*-propyl ether (BIRCH and NORRIS), 904.

$C_6H_{15}P$ Triethylphosphine, preparation and reactions of (COLLIE), 964.

6 III

$C_6H_3O_{12}Al$ Aluminioxalic acid, salts of, with optically active bases (CHILD, ROBERTS, and TURNER), 2971.

$C_6H_3O_{12}Sb$ Antimonoxalic acid, potassium salt (HOLMES and TURNER), 1753.

$C_6H_3Cl_3S$ 2:5-Dichlorophenylsulphur chloride (MILLER and SMILES), 230.

$C_6H_3FeN_6$ Hydroferricyanic acid, potassium salt, oxidation of carbohydrates by (KNECHT and HIBBERT), 2854.

C_6H_4ClAs *p*-Chlorophenyldichloroarsine (HUNT and TURNER), 2671.

C_6H_5ON Nitrosobenzene, bromination and nitration of (INGOLD), 515.

$C_6H_5O_2N$ Nitrobenzene, dielectric constant of (HARRIS), 1067; cryoscopy with (BROWN), 345.

$C_6H_6O_2Ge$ Phenylgermanonic acid (MORGAN and DREW), 1764.

$C_6H_6N_2Br_2$ 2:4-Dibromophenylhydrazine, preparation of (HUMPHRIES and EVANS), 1676.

$C_6H_9O_3N$ β-Ethylcarbonatopropionitrile (CHAPMAN and STEPHEN), 888.

$C_6H_{11}ON$ α-Ethylcrotonamides (NEWBERY), 301.

Methylpentenoic amides (KON and LINSTEAD), 623.

$C_6H_{11}O_3N$ Methoxymethylanthranilic acids (HEILBRON, KITCHEN, PARKES, and SUTTON), 2173.

$C_6H_{12}O_2N_2$ Malonmono*iso*propylamide (WEST), 750.

$C_6H_{12}O_3S$ *cyclo*Hexanesulphonic acid, salts of (KOLKER and LAPWORTH), 312.

$C_6H_{12}Cl_2S$ γγ′-Dichlorodipropyl sulphide, and its platinic chloride additive compound (BENNETT and HOCK), 2674.

$C_6H_{13}ClS$ Pentamethylenemethylsulphonium chloride (THIERRY), 2759.

6 IV

$C_6H_2O_7N_3Cl$ 3-Chloro-2:5:6-trinitrophenol (HODGSON and MOORE), 1603.

C_6H_4OClAs *p*-Chlorophenylarsenious oxide (HUNT and TURNER), 2671.

C_6H_4OBrAs *p*-Bromophenylarsenious oxide (HUNT and TURNER), 2670.

$C_6H_4O_3NBr$ 3-Bromo-*p*-benzoquinone-4-oxime (HODGSON and MOORE), 2261.

Bromonitrosophenols (HODGSON and MOORE), 2261.

$C_6H_4O_3NI$ 3-Iodo-*p*-benzoquinone-4-oxime (HODGSON and MOORE), 2262.

2-Iodo-4-nitrosophenol (HODGSON and MOORE), 2264.

$C_6H_4O_3NCl$ 3-Chloro-2-nitrophenol, and its silver salt (HODGSON and MOORE), 1600.

$C_6H_4O_3NBr$ 3-Bromo-4-nitrophenol (HODGSON and MOORE), 2262.

$C_6H_4O_3NI$ 3-Iodo-4-nitrophenol (HODGSON and MOORE), 2263.

$C_6H_4Cl_2BrAs$ *p*-Bromophenyldichloroarsine (HUNT and TURNER), 2670.

C_6H_6ONBr *p*-Bromophenylhydroxylamine, preparation of (HAWORTH and LAPWORTH), 2970.

$C_6H_{10}O_2N_2Te$ 2-Methyl*cyclo*telluropentane-3:5-dione dioxime (MORGAN and KELLETT), 2621.

$C_6H_{10}O_5N_3I$ 4(5)-Nitrotrimethylglyoxalinium iodides (BHAGWAT and PYMAN) 1834.

$C_6H_{10}O_2Cl_2Te$ Tellurium bisacetone dichloride (MORGAN and ELVINS), 2628.

$C_6H_{10}O_4NCl$ Ethyl α-chloronitrobutyrate (MACBETH and TRAILL), 897.

$C_6H_{10}O_4NBr$ Ethyl α-bromonitrobutyrate (MACBETH and TRAILL), 897.

$C_6H_{11}ONBr_2$ αβ-Dibromo-α-ethylbutyramides (NEWBERY), 304.

$C_6H_{11}OCl_3Te$ Tellurium pinacolin trichloride (MORGAN and ELVINS), 2630.

$C_6H_{11}O_2N_2Br$ Bromomalonmono*iso*propylamide (WEST), 752.

$C_6H_{12}O_2Cl_2S$ γγ′-Dichlorodipropylsulphone (BENNETT and HOCK), 2675.

$C_6H_{12}Cl_2Br_2S$ γγ′-Dichlorodipropyl sulphide dibromide (BENNETT and HOCK), 2674.

$C_6H_{14}O_2S_2Hg$ γ-Hydroxypropyl mercaptan mercaptide (BENNETT and HOCK), 2673.

$C_6H_{18}Cl_2Sb_2Pd$ Bistrimethylstibinedichloropalladium (MORGAN and YARSLEY), 190.

$C_6H_{18}Cl_2Sb_2Pt$ Bistrimethylstibinedichloroplatinum (MORGAN and YARSLEY), 188.

6 V

$C_6H_3O_2Cl_2IS$ 2:5-Dichlorobenzenesulphonyl iodide (GIBSON, MILLER, and SMILES), 1823.

C_7 Group.

C_7H_8 Toluene, catalytic chlorination of (O. and C. A. SILBERRAD and PARKE), 1724; mercuration of (COFFEY), 1029.

7 II

$C_7H_6O_2$ Benzoic acid, periodic crystallisation of (HEDGES and MYERS), 2434.

$C_7H_6O_3$ Salicylic acid, heat of combustion of (BERNER), 2747; equilibrium of phenol, water, and (BAILEY), 1951.

$C_7H_8O_2$ Resorcinol methyl ether, thallous salt (CHRISTIE and MENZIES), 2373.

$C_7H_8O_4$ Heptodilactone (BENNETT), 1277.

3-Methoxy-3-methyl*cyclo*propane-1:2-dicarboxylic anhydride (GOSS, INGOLD, and THORPE), 468.

Methyl hydrogen 3-methyl-Δ^2-*cyclo*propene-1:2-dicarboxylate (GOSS, INGOLD, and THORPE), 467.

$C_7H_8O_6$ αγ-Dialdehydopropane-ββ-dicarboxylic acid (PERKIN and PINK), 193.

$C_7H_{10}O_6$ *as*-Dimethylcarboxysuccinic acid (INGOLD), 473.

$C_7H_{10}N_2$ 3-Amino-2:6-lutidine, and its hydrochloride (GULLAND and ROBINSON), 1495.

$C_7H_{12}O$ Methyl αγ-dimethoxyacetoacetate (PRATT and ROBINSON), 169.

$C_7H_{12}O_2$ ββ-Dimethyl-α-ethylacrylic acid (KON, SMITH, and THORPE), 572.

Ethylpentenoic acids (KON and LINSTEAD), 621.

$C_7H_{12}O_4$ Diethyl malonate, addition of, to esters (WAYNE and COHEN), 450.

$C_7H_{14}O$ *n*-Butylvinylcarbinol, resolution and rotation of (KENYON and SNELLGROVE), 1177.

$C_7H_{15}I$ Triethylcarbinyl iodide (MORGAN, CARTER, and DUCK), 1253.

7 III

$C_7H_5O_2Br$ Bromohydroxybenzaldehydes (HODGSON and BEARD), 878.

$C_7H_5O_2Li$ Lithium salicylaldehyde ($+2H_2O$) (SIDGWICK and BREWER), 2385.

$C_7H_5O_2Na$ Sodium salicylaldehyde ($+2H_2O$) (SIDGWICK and BREWER), 2385.

$C_7H_5O_6N_3$ Trinitrotoluene, equilibrium of naphthalene and, in nitrobenzene (BROWN), 345.

$C_7H_5O_7N_3$ Trinitroanisole, alcoholysis of (BRADY and HORTON), 2230.

$C_7H_6O_4N_2$ Nitrohydroxybenzaldoximes (HODGSON and BEARD), 879.

C_7H_7OBr 2-Bromo-*m*-cresol, preparation of (HODGSON and BEARD), 498.

Phenacyl bromide, condensation reactions of (R. M. and J. N. RÂY), 2721.

C_7H_7OTl Thallous *m*-tolyloxide (CHRISTIE and MENZIES), 2373.

$C_7H_7O_2N$ *o*-Nitrotoluene, dielectric constant of (HARRIS), 1067.

$C_7H_8O_2N_2$ Nitrobenzylamines, and their salts (HOLMES and INGOLD), 1812.

C_7H_9ON 2-Amino-*m*-cresol, preparation of (HODGSON and BEARD), 498.

$C_7H_9O_2N$ 3:4-Dihydroxybenzylamine (JONES and PYMAN), 2596.

$C_7H_9O_4Br$ Methyl 1-bromo*cyclo*propane-1:2-dicarboxylate (ING and PERKIN), 2396.

$C_7H_9N_2Cl$ 5-Chloro-2-methyl-*p*-phenylenediamine (KENNER, TOD, and WITHAM), 2347.

$C_7H_{10}O_4Cl_2$ Di-β-chloroethyl malonate (BENNETT), 1278.

$C_7H_{10}O_4Br_2$ Methyl αα′-dibromoglutarates (ING and PERKIN), 2393.

$C_7H_{10}O_4I_2$ Methyl αα′-di-iodoglutarate (ING and PERKIN), 2393.

$C_7H_{11}ON_3$ 2-Acetylamino-4:5-dimethylglyoxaline (BURTLES and PYMAN), 2016.

$C_7H_{12}O_2N_2$ α-Ethylcrotonylcarbamides (NEWBERY), 300.

$C_7H_{12}N_2S$ 2-Ethylthiol-1:4-dimethylglyoxaline, salts of (BURTLES, PYMAN, and ROYLANCE), 588.

$C_7H_{13}ON$ Amides of ethylpentenoic acids (KON and LINSTEAD), 621.

$C_7H_{13}O_5I$ Methylglucoside 6-iodohydrin (OLDHAM), 2844.

$C_7H_{13}O_8N$ Methylglucoside 6-nitrate (OLDHAM), 2844.

$C_7H_{14}O_2N_2$ Malonmono*iso*butylamide (WEST), 750.

$C_7H_{17}O_3N$ α-Aminopropionacetal (BURTLES, PYMAN, and ROYLANCE), 586.

7 IV

$C_7H_3O_2NCl_4$ 2:3:4:6-Tetrachloro-3-nitrotoluene (SILBERRAD), 2683.

$C_7H_5O_2NBr_2$ 4:6-Dibromo-3-hydroxybenzaldoxime (HODGSON and BEARD), 880.

$C_7H_5O_3N_2Cl$ 2-Chloro-5-nitrobenzaldoximes (BRADY and BISHOP), 1361.

$C_7H_5O_3Cl_2S$ 4-Chloroanisole-2-sulphonyl chloride (GAUNTLETT and SMILES), 2745.

$C_7H_5O_4N_2Cl$ 4-Chloro-2:3-dinitrotoluene (KENNER, TOD, and WITHAM), 2348.

$C_7H_5O_5N_2Na$ Sodium dinitro-*o*-tolyl oxide (GIBSON), 45.

C_7H_6ONBr *o*-Bromo-β-benzaldoxime (BRADY, COSSON, and ROPER), 2430.

$C_7H_6O_2NBr$ Bromohydroxybenzaldoximes (HODGSON and BEARD), 879.

$C_7H_6O_2Cl_2S$ 2:5-Dichlorophenylmethylsulphone (MILLER and SMILES), 231.

$C_7H_6O_3NCl$ 3-Chloro-2-nitrophenol methyl ether (HODGSON and MOORE), 1601.

$C_7H_6O_3NNa$ Sodium nitro-*o*-tolyl oxides (GIBSON), 45.

C_7H_7OClS 4-Chloroanisole-2-mercaptan (GAUNTLETT and SMILES), 2746.

$C_7H_7O_3N_2Cl$ Chloronitrotoluidines (KENNER, TOD, and WITHAM), 2346.

$C_7H_7O_2ClS$ 4-Chlorophenylmethylsulphone (MILLER and SMILES), 231.

$C_7H_7O_2Cl_3Te$ 2-Hydroxy-1-methoxyphenyl-4-telluritrichloride (MORGAN and DREW), 2314.

$C_7H_7O_2BrS$ 3- and 4-Bromophenylmethylsulphones (TWIST and SMILES), 1252.

$C_7H_7O_3ClS$ 4-Chloroanisole-2-sulphinic acid (GAUNTLETT and SMILES), 2746.

$C_7H_7O_4NS$ 3-Nitrophenylmethylsulphone (TWIST and SMILES), 1250.

$C_7H_7O_4ClS_2$ *m*-Chlorosulphonylphenylmethylsulphone (TWIST and SMILES), 1251.

C_7H_7BrIAs *p*-Bromophenylmethyliodoarsine (HUNT and TURNER), 2670.

C_7H_8ONBr 4-Bromo-*m*-anisidine (GRIFFITH and HOPE), 994.

$C_7H_{10}O_6NCl$ Ethyl chloronitromalonate (MACBETH and TRAILL), 1121.

$C_7H_{12}O_2N_2Br_2$ αβ-Dibromo-α-ethylbutyrylcarbamides (NEWBERY), 305.

$C_7H_{12}O_2N_2Te$ 2:6-Dimethyl*cyclo*telluropentane-3:5-dionedioxime (MORGAN and TAYLOR), 799.

$C_7H_{12}O_2Cl_4Te_2$ Methylenebistelluriacetone dichloride (MORGAN and DREW), 537.

$C_7H_{13}OCl_3Te$ Tellurium di-*n*-propylketone trichloride (MORGAN and ELVINS), 2629.

$C_7H_{13}O_3N_2Br$ α-Bromo-α-ethylbutyrylcarbamide, action of alkalis on (NEWBERY), 295.

β-Bromo-α-ethylbutyrylcarbamide (NEWBERY), 305.

Bromomalonmono*iso*butylamide (WEST), 751.

$C_7H_{14}ON_2S$ 2-Methylamino-5-ethoxy-4-methyl-4:5-dihydrothiazole, and its salts (BURTLES, PYMAN, and ROYLANCE), 586.

7 V

$C_7H_4NClBr_2S$ Chlorobenzthiazole dibromide (HUNTER), 1488.

$C_7H_7ONClBr$ *o*-Bromo-α-benzaldoxime hydrochloride (BRADY, COSSON, and ROPER), 2430.

$C_7H_7O_4ClSNa$ 4-Chloroanisole-2-sulphonic acid, sodium salt (GAUNTLETT and SMILES), 2745.

$C_7H_{15}Cl_2I_3SHg$ Dichlorodipropylmethylsulphonium mercuri-iodide (BENNETT and HOCK), 2675.

C_8 Group.

$C_8H_6O_4$ *m*-Aldehydophenyl carbonate, nitration of (MASON), 1195.

$C_8H_8O_3$ Vanillin, thallous salt (CHRISTIE and MENZIES), 2373.

$C_8H_8O_7$ Diacetyltartaric anhydride, mutarotation of (AUSTIN and PARK), 1926.

$C_8H_{10}O_4$ Ethyl hydrogen 3-methyl-Δ^2-*cyclo*propene-1:2-dicarboxylate (GOSS, INGOLD, and THORPE), 468.

$C_8H_{10}O_8$ Diacetyltartaric acid, rotatory dispersion of (AUSTIN and PARK), 1926.

$C_8H_{11}N$ Phenylethylamine, condensation of *s*-dichloromethyl ether with (SHORT), 269.

l-Phenylethylamine, aluminioxalate of (CHILD, ROBERTS, and TURNER), 2972.

$C_8H_{14}O_2$ 3-Methyldipropionylmethane, and its copper salt (MORGAN and TAYLOR), 799.

$C_8H_{14}O_5$ Ethyl αγ-dimethoxyacetoacetate (PRATT and ROBINSON), 168.

Ethyl β-ethylcarbonatopropionate (CHAPMAN and STEPHEN), 889.

Acid, from sodium ethoxide and ethyl α-chloro-γ-methylglutarate (GOSS and INGOLD), 2779.

$C_8H_{14}O_6$ Trimethylarabonolactones (PRYDE, HIRST, and HUMPHREYS), 354.

$C_8H_{16}O_5$ Trimethyl γ-arabinose (BAKER and HAWORTH), 368.

8 III

$C_8H_5O_2N$ Isatin, absorption spectra of (MORTON and ROGERS), 2698.

$C_8H_6O_3Br_2$ 4:6-Dibromo-3-methoxybenzaldehyde (HODGSON and BEARD), 879.

$C_8H_6Cl_3As$ α-Chlorostyryldichloroarsine (HUNT and TURNER), 998.

$C_8H_7O_2N$ 1-Hydroxy-2:3-benzoxazine (GRIFFITHS and INGOLD), 1704.

1-Hydroxy*iso*indole-2-oxide (GRIFFITHS and INGOLD), 1706.

$C_8H_7O_3Br$ 3-Bromo-2-hydroxy-5-methoxybenzaldehyde (RUBENSTEIN), 2001.

Bromomethoxybenzoic acids (HODGSON and BEARD), 880.

$C_8H_7O_3Li$ Lithium methyl salicylate (+ $2H_2O$) (SIDGWICK and BREWER), 2384.

$C_8H_7O_5N$ 3-Nitro-2-hydroxy-5-methoxybenzaldehyde (RUBENSTEIN), 2000.

5-Nitro-2-hydroxy-4-methoxybenzaldehyde (RAO, SRIKANTIA, and IYENGAR), 557.

$C_8H_7O_7N_3$ Trinitrophenetole, alcoholysis of (BRADY and HORTON), 2230.

$C_8H_7Cl_2As$ Phenyl-β-chlorovinylchloroarsine (HUNT and TURNER), 997.

$C_8H_8O_2Se$ Phenylselenoglycollic acid (MORGAN and PORRITT), 1757.

$C_8H_8O_3N$ Phthalamic acid, ammonium salt (CHAPMAN and STEPHEN), 1793.

$C_8H_8O_3N_2$ 3-Nitro-4-methylbenzaldoximes (BRADY, COSSON, and ROPER), 2432.

C_8H_5OBr 2-Bromoanisic acid (GRIFFITH and HOPE), 993.

$C_8H_{10}O_2N_2$ 3-Amino-2:6-dimethyl*iso*nicotinic acid, and its salts (GULLAND and ROBINSON), 1494.

Benzylmethylamines, nitro-, and their hydrochlorides (HOLMES and INGOLD), 1814.

α-Hydroxybenzylcarbamide, and its salts (WOOD and LILLEY), 97.

$C_8H_{10}O_2S_2$ *m*-Methylthiolphenylmethylsulphone (TWIST and SMILES), 1251.

$C_8H_{10}O_4N_2$ 4-Nitro-2:5-dimethoxyaniline, hydrochloride of (RUBENSTEIN), 2004.

$C_8H_{10}IAs$ *p*-Tolylmethyliodoarsine (MILLS and RAPER, 2481.

$C_8H_{11}ON$ α-Hydroxybenzylmethylamine (WOOD and LILLEY), 96.

$C_8H_{12}O_2Te$ 2:4:6-Trimethyl*cyclo*telluropentane-3:5-dione (MORGAN and TAYLOR), 800.

$C_8H_{13}O_4Cl$ Methyl γ-chloro-α-methylglutarate (INGOLD), 393.

$C_8H_{13}O_4Br$ Methyl γ-bromo-α-methylglutarate (INGOLD), 393.

$C_8H_{13}O_4I$ Methyl α-iodo-α-methylglutarate (INGOLD), 394.

$C_8H_{14}O_2Br_2$ Ethyl αε-dibromopentane-γ-carboxylate (MILLS and BAINS), 2505.

$C_8H_{16}O_2N_2$ Malonmonoethylmono*iso*propylamide (WEST), 750.

$C_8H_{16}O_2N_2$ Trimethoxyglutardiamide (HIRST and ROBERTSON), 362.

$C_8H_{16}O_{10}N_2$ 2:3:5-Trimethyl glucose 1:6-dinitrate (OLDHAM), 2841.

$C_8H_{17}O_2N$ α-Ethoxy-α-ethylbutyramide (NEWBERY), 307.

$C_8H_{19}O_2N$ α-Methylaminopropionacetal (BURTLES, PYMAN, and ROYLANCE), 586.

8 IV

$C_8H_3O_3NBr_2$ 4:5-Dibromophthalamic acid, and its ammonium salt (CHAPMAN and STEPHEN), 1794.

$C_8H_6O_2N_2S$ Nitrobenzyl thiocyanates (FOOTNER and SMILES), 2890.

$C_8H_7O_2BrSe$ *p*-Bromophenylselenoglycollic acid (MORGAN and PORRITT), 1757.

$C_8H_7O_2Br_3Se$ *p*-Bromophenylselenoglycollic acid dibromide (MORGAN and PORRITT), 1759.

$C_8H_7O_2Br_5Se$ *p*-Bromophenylselenoglycollic acid tetrabromide (MORGAN and PORRITT), 1759.

$C_8H_7O_3BrSe$ *p*-Bromophenylselenoxyglycollic acid (MORGAN and PORRITT), 1758.

$C_8H_8ON_2Br_2$ Acetyl-2:4-dibromophenylhydrazine, and its hydrobromide (HUMPHRIES and EVANS), 1677.

$C_8H_8O_2NBr$ 6-Bromo-3-methoxybenzaldoxime (HODGSON and BEARD), 880.

$C_8H_8O_3NCl$ 4-Chloro-6-nitro-*m*-tolyl methyl ether (KENNER, TOD, and WITHAM), 2348.

$C_8H_8O_3NBr$ 5-Bromo-2-amino-4-methoxybenzoic acid, and its salts (GRIFFITH and HOPE), 994.

$C_8H_9ON_2Br$ Acetyl-*p*-bromophenylhydrazine, and its hydrobromide (HUMPHRIES and EVANS), 1676.

$C_8H_9OCl_3Te$ *p*-Phenetyltelluritrichloride (MORGAN and DREW), 2311.

$C_8H_9O_2Cl_3Te$ 1:3-Dimethoxyphenyl-4-telluritrichloride (MORGAN and DREW), 2312.

$C_8H_9O_3N_2Cl$ 3-Nitro-4-methyl-β-benzaldoximehydrochloride (BRADY, COSSON, and ROPER), 2432.

$C_8H_9O_3ClS$ 4-Chloroanisole-2-methylsulphone (GAUNTLETT and SMILES), 2746.

$C_8H_{10}ONCl$ 5-Chloro-2-amino-4-methoxytoluene (HEILBRON, KITCHEN, PARKES, and SUTTON), 2175.

$C_8H_{10}OI_2Te$ *p*-Anisylmethyltelluridi-iodide (MORGAN and DREW), 2315.

$C_8H_{12}O_2Cl_2Te$ 2:4:6-Trimethyl*cyclo*telluripentane-3:5-dione 1:1-dichloride (MORGAN and TAYLOR), 800.

$C_8H_{13}O_2NTe$ 2-Methyl-4-ethyl*cyclo*telluropentane-3:5-dione monoxime (MORGAN and KELLETT), 2622.

$C_8H_{14}O_2N_2Te$ 2-Methyl-4-ethyl*cyclo*telluropentane-3:5-dione dioxime (MORGAN and KELLETT), 2622.

2:4:6-Trimethyl*cyclo*telluropentane-3:5-dionedioxime (MORGAN and TAYLOR), 800.

$C_8H_{15}O_2N_2Br$ Bromomalonmonoethylmono*iso*propylamide (WEST), 752.

$C_8H_{20}I_2S_4Cu_2$ Dimethyldithiolethylene cuprous iodide (MORGAN, CARTER, and HARRISON), 1922.

C_9 Group.

C_9H_{20} 3:3-Diethylpentane (MORGAN, CARTER, and DUCK), 1252.

9 II

$C_9H_6O_3$ 4-Aldehydo-1:2-phthalide (PERKIN and STONE), 2290.
$C_9H_6O_4$ 4-Carboxy-1:2-phthalide (PERKIN and STONE), 2291.
2:4-Dialdehydobenzoic acid (PERKIN and STONE), 2292.
$C_9H_6O_5$ 2-Aldehydoterephthalic acid (PERKIN and STONE), 2294.
C_9H_8O Cinnamaldehyde, action of, on Grignard reagents (MARSHALL), 2186.
$C_9H_8O_2$ 4-Methyl-1:2-phthalide (PERKIN and STONE), 2285.
$C_9H_8O_3$ Hydroxy-3:4-dihydrocoumarins (CHAPMAN and STEPHEN), 890.
4-Hydroxymethyl-1:2-phthalide (PERKIN and STONE), 2287.
$C_9H_8O_5$ 2-Hydroxymethylterephthalic acid (PERKIN and STONE), 2291.
$C_9H_9N_3$ Aminophenylglyoxalines, and their salts (BALABAN and KING), 2710.
$C_9H_{10}O_2$ 2:4-Dimethylbenzoic acid (PERKIN and STONE), 2283.
$C_9H_{10}O_3$ Ethyl acetoacetate, thallous salt (CHRISTIE and MENZIES), 2372.
Hydroxydimethylbenzoic acids (PERKIN and STONE), 2285.
4-Methoxy-3-methylbenzoic acid (BRADY, COSSON, and ROPER), 2431.
$C_9H_{10}O_4$ *m*-Aldehydophenyl ethyl carbonate, nitration of (MASON), 1195.
2:4-Di(hydroxymethyl)benzoic acid (PERKIN and STONE), 2287.
β-2:6-Dihydroxyphenylpropionic acid (CHAPMAN and STEPHEN), 891.
$C_9H_{10}Br_2$ αγ-Dibromo-β-phenylpropane (MILLS and BAINS), 2505.
$C_9H_{12}O_2$ Benzyl hydroxyethyl ether (BENNETT), 1279.
$C_9H_{12}O_4$ Methyl ethyl 3-methyl-Δ^2-*cyclo*propene-1:2-dicarboxylate (GOSS, INGOLD, and THORPE), 468.
Nonodilactone (BENNETT), 1278.
$C_9H_{14}O_2$ Acetylmethyl*cyclo*hexanone, beryllium salt (MORGAN and ELVINS) 2624.
α-Campholytic acid, structure of (CHANDRASENA, INGOLD, and THORPE), 1677.
1-Methyl*cyclo*hexylidene-4-acetic acid, rotatory dispersion of (RICHARDS and LOWRY), 238.
$C_9H_{14}O_3$ 1-Methyl*cyclo*hexan-3-one-1-acetic acid, and its silver salt (FARMER and ROSS), 2365.
Lactone, from *Alstonia* bark (GOODSON and HENRY), 1647.
$C_9H_{14}O_5$ Acid, and its salts, from chenopodium oil (HENRY and PAGET), 1653.
$C_9H_{16}O_2$ 3-Butylacetylacetones, and their salts (MORGAN and JONES), 2618.
Di*iso*butyrylmethane, and its copper salt (MORGAN and TAYLOR), 803.
Ethyl ethylpentenoates (KON and LINSTEAD), 622.
3-*n*- and -*iso*-Propylpropionylacetones (MORGAN and CORBY), 2616.
$C_9H_{16}O_3$ β-*iso*Valeryl-α-methylpropionic acid (JONES and SMITH), 2536.
$C_9H_{18}O_4$ Ethyl ββ-diethoxypropionate (INGOLD), 1203.
$C_9H_{18}O_5$ Trimethyl γ-methylarabinoside (BAKER and HAWORTH), 367.
$C_9H_{18}O_6$ Dimethyl methylglucoside (IRVINE and OLDHAM), 2920.
Glycerolglucoside (GILCHRIST and PURVES), 2735.
Trimethylglucose, synthesis of (IRVINE and OLDHAM), 2729.

9 III

$C_9H_3OCl_7$ 2:4-Di(trichloromethyl)benzoyl chloride (PERKIN and STONE), 2295.
$C_9H_3O_2Cl_5$ 4-Trichloromethyl-1:2-phthalyl chloride (PERKIN and STONE), 2296.
$C_9H_4OCl_6$ Pentachloro-2:4-dimethylbenzoyl chlorides (PERKIN and STONE), 2293.
$C_9H_4O_2Cl_6$ 2:4-Di(trichloromethyl)benzoic acid (PERKIN and STONE), 2296.
$C_9H_5OCl_5$ 2:4-Di(dichloromethyl)benzoyl chloride (PERKIN and STONE), 2291.

$C_9H_5O_2Cl_3$ 4-Dichloromethyl-1:2-chlorophthalide (PERKIN and STONE), 2292.
$C_9H_6OCl_4$ Trichlorodimethylbenzoyl chloride (PERKIN and STONE), 2289.
$C_9H_6O_2Cl_4$ 2:4-Di(dichloromethyl)benzoic acid (PERKIN and STONE), 2291.
$C_9H_6N_2Br_2$ 2:5(2:4)-Dibromo-4(5)-phenylglyoxaline (FORSYTH and PYMAN), 578.
C_9H_7ON Carbostyril, absorption spectra of (MORTON and ROGERS), 2698.
$C_9H_7ON_6$ 2-Methylpyridine-3:4:6-tricarboxylic acid, thallous salt (CHRISTIE and MENZIES), 2371.
$C_9H_7OBr_3$ 2:4-Di(bromomethyl)benzoyl bromide (PERKIN and STONE), 2286.
$C_9H_7O_2N$ *o*-Methoxybenzoyl cyanide (MARSH and STEPHEN), 1635.
$C_9H_7O_2Cl$ 4-Chloromethyl-1:2-phthalide (PERKIN and STONE), 2289.
$C_9H_7O_2Br$ 4-Bromomethyl-1:2-phthalide (PERKIN and STONE), 2287.
$C_9H_7O_3N$ Methylisatoic anhydride (HEILBRON, KITCHEN, PARKES, and SUTTON), 2171.
$C_9H_7O_5N$ 2-Aldehydoterephthalic acid oxime (PERKIN and STONE), 2294.
$C_9H_7N_2Br$ Bromophenylglyoxalines, and their salts (FORSYTH and PYMAN), 576.
$C_9H_8OBr_2$ Bromodimethylbenzoyl bromides (PERKIN and STONE), 2284.
$C_9H_8O_2Br_2$ 2:4-Di(bromomethyl)benzoic acid (PERKIN and STONE), 2286.
$C_9H_8O_4N_2$ Acetyl-*o*-nitro-*β*-benzaldoxime (BRADY and MCHUGH), 2423.
$C_9H_8O_5N$ Dinitromethoxystyrene (C. K. and E. H. INGOLD), 872.
$C_9H_8O_5N_2$ 3-Nitro-2-acetylaminobenzoic acid (CHAPMAN and STEPHEN), 1795.
$C_9H_8O_6N_2$ 3:5-Dinitro-*o*-tolyl acetate (GIBSON), 46.
C_9H_9ON 4-Methoxy-3-methylbenzonitrile (BRADY, COSSON, and ROPER), 2431.
o-Methylphthalimidine (GRIFFITHS and INGOLD), 1708.
C_9H_9OCl 2:4-Dimethylbenzoyl chloride, action of halogens on (PERKIN and STONE), 2275.
$C_9H_9O_2N$ 6-Hydroxy-4-keto-1:2:3:4-tetrahydroquinoline (CLEMO and PERKIN), 2307.
1-Methoxy-2:3-benzoxazine (GRIFFITHS and INGOLD), 1704.
Methoxy*iso*indole 2-oxide (GRIFFITHS and INGOLD), 1708.
N-Methoxyphthalimidine (GRIFFITHS and INGOLD), 1707.
$C_9H_9O_2Cl$ *o*-Acetoxybenzyl chloride (GRAY), 1155.
r-*β*-Chlorohydratropic acid, resolution of (MCKENZIE and STRATHERN), 86.
$C_9H_9O_2Br$ Bromodimethylbenzoic acid (PERKIN and STONE), 2284.
β-Bromo-*β*-phenylpropionic acid, ammonium salt (SENTER and WARD), 1849.
$C_9H_9O_3Br$ Bromo-2:5-dimethoxybenzaldehydes (RUBENSTEIN), 2001.
$C_9H_9O_4N$ Nitro-*o*-tolyl acetates (GIBSON), 46.
$C_9H_9O_5N$ Nitro-2:5-dimethoxybenzaldehydes (RUBENSTEIN), 2000.
3-Nitro-4-ethoxybenzoic acid (KING and MURCH), 2645.
Acid, and its salts from oxidation of ethoxylutidine (COLLIE and BISHOP), 963.
$C_9H_{10}O_2N_2$ Methoxy-2-methyl-4-quinazolones (HEILBRON, KITCHEN, PARKES, and SUTTON), 2173.
$C_9H_{10}O_2N_4$ Phthalaldehyde 1-oxime-2-semicarbazone (GRIFFITHS and INGOLD), 1704.
$C_9H_{10}O_2Se$ *p*-Tolylselenoglycollic acid (MORGAN and PORRITT), 1758.
$C_9H_{10}O_3Se$ *p*-Tolylselenoxyglycollic acid (MORGAN and PORRITT), 1758.
$C_9H_{10}O_5N_2$ Acid, and its silver salt from oxidation of nitroethoxylutidine (COLLIE and BISHOP), 963.
$C_9H_{10}O_6N_2$ Trimethylene glycol mono-2:4-dinitrophenyl ether (FAIRBOURNE and FOSTER), 2761.
$C_9H_{11}ON$ Hydroxyhydrindamine, chlorobromomethanesulphonates (READ and MCMATH), 1587.
$C_9H_{11}OCl$ Benzyl chloroethyl ether (BENNETT), 1280.

$C_9H_{11}O_2N$ 4-Methoxy-3-methylbenzaldoximes (BRADY, COSSON, and ROPER), 2431.

$C_9H_{11}O_3Br$ 2:3-Dimethoxybenzyl bromide (HAWORTH and PERKIN), 1437.
3:4-Dimethoxybenzyl bromide (HAWORTH, PERKIN, and RANKIN), 1445.

$C_9H_{12}O_2N_2$ Methoxymethylanthranilamides (HEILBRON, KITCHEN, PARKES, and SUTTON), 2174.

$C_9H_{12}O_3N_2$ Nitroethoxylutidine (COLLIE and BISHOP), 962.

$C_9H_{12}O_4N$ 3-Amino-2:5-dimethoxybenzoic acid, and its hydrochloride (RUBENSTEIN), 2002.

$C_9H_{12}O_4Br_2$ Methyl ethyl 2:3-dibromo-3-methyl*cyclo*propane-1:2-dicarboxylate (GOSS, INGOLD, and THORPE), 468.

$C_9H_{14}ON_2$ Aminoethoxylutidine, and its salts (COLLIE and BISHOP), 962.

$C_9H_{14}O_2Te$ 4-*iso*Butyl*cyclo*telluropentane-3:5-dione (MORGAN and JONES), 2619.
4-*sec.*-Butyl*cyclo*telluropentane-3:5-dione (MORGAN and ELVINS), 2623.
2-Methyl-4-propyl*cyclo*telluropentane-3:5-diones (MORGAN and CORBY), 2616.

$C_9H_{14}O_4Br_2$ $\alpha\gamma$-Dibromo-$\beta\beta$-dimethyl-α-ethylglutaric acids (KON, SMITH, and THORPE), 571.

$C_7H_{16}O_6N_2$ Ethyl hydrazotricarboxylate (INGOLD and WEAVER), 381.

$C_9H_{17}ON_3$ δ-Ethylhexenone semicarbazones (KON and LINSTEAD), 818.

$C_9H_{18}O_2N_2$ Malondi*iso*propylamide (WEST), 750.

$C_9H_{19}ON$ α-*iso*Propyl-*n*-hexoamide (JONES and PYMAN), 2597.

9 IV

$C_9H_5ONCl_6$ 2:4-Di(trichloromethyl)benzamide (PERKIN and STONE), 2296.

$C_9H_7O_3NBr_2$ 4:5-Dibromo-2-acetylaminobenzoic acid (CHAPMAN and STEPHEN), 1794.

$C_9H_7O_4N_2Cl$ α-Acetyl-2-chloro-5-nitrobenzaldoxime (BRADY and BISHOP), 1361.

$C_9H_8O_2NBr$ Acetyl-*o*-bromo-α-benzaldoxime (BRADY, COSSON, and ROPER), 2429.

$C_9H_9OCl_3Te$ Tellurium phenylethylketone trichloride (MORGAN and ELVINS), 2631.

$C_9H_9O_3N_2Cl$ Acetylchloronitrotoluidines (KENNER, TOD, and WITHAM), 2346.

$C_9H_{10}O_2Br_2Se$ *p*-Tolylselenoglycollic acid dibromide (MORGAN and PORRITT), 1759.

$C_9H_{10}O_2Br_4Se$ *p*-Tolylselenoglycollic acid tetrabromide (MORGAN and PORRITT), 1759.

$C_9H_{13}OITe$ *p*-Anisyldimethyltelluri-iodide (MORGAN and DREW), 2314.

$C_9H_{14}O_2Cl_2Te$ 2-Methyl-4-propyl*cyclo*telluripentane-3:5-dione dichlorides (MORGAN and CORBY), 2616.

$C_9H_{17}O_2N_2Br$ Bromomalondi*iso*propylamide (WEST), 751.

$C_9H_{24}O_2Cl_2Te$ 4-*iso*Butyl*cyclo*telluripentane-3:5-dione 1:1-dichloride (MORGAN and JONES), 2619.

C_{10} Group.

$C_{10}H_8$ Naphthalene, equilibria of, in nitrobenzene solution (BROWN), 345.

$C_{10}H_{16}$ Limonene, action of hydrogen peroxide on (SWORD), 1632.
Sylvestrene, occurrence of (RAC and SIMONSEN), 2494.

$C_{10}H_{18}$ Decahydronaphthalene, isomerism of (WIGHTMAN), 1421.

10 II

$C_{10}H_8O_4$ 1:2-Phthalide-4-acetic acid (PERKIN and STONE), 2288.

$C_{10}H_{10}O_2$ Benzoylacetone, thallous salt (CHRISTIE and MENZIES), 2372.

$C_{10}H_{10}O_3$ Phenyl α-methoxy-β-hydroxyvinyl ketone (MALKIN and ROBINSON), 1192.

$C_{10}H_{10}O_4$ *m*-Meconine, preparation and nitration of (RÂY and ROBINSON), 1618.

$C_{10}H_{10}O_4$ Meconines, synthesis of (EDWARDS, PERKIN, and STOYLE), 195.
$C_{10}H_{10}O_5$ 4-Ethylcarbonatobenzoic acid (KING and MURCH), 2649.
$C_{10}H_{10}N_2$ 2-Phenyl-1-methylglyoxaline, and its salts (BALABAN and KING), 2714.
$C_{10}H_{11}N$ 1:2-Dihydroquinaldine, synthesis of (MASON), 1032.
$C_{10}H_{12}O$ 2:4-Dimethylacetophenone (PERKIN and STONE), 2283.
$C_{10}H_{12}O_2$ Methyl 2:4-dimethylbenzoate (PERKIN and STONE), 2284.
$C_{10}H_{12}O_3$ Dimethoxyacetophenones (PRATT and ROBINSON), 1184.
$C_{10}H_{12}Br$ $\alpha\gamma$-Dibromo-β-phenyl-β-methylpropane (MILLS and BAINS), 2504.
$C_{10}H_{13}Br$ β-Bromo-α-phenyl-β-methylpropane (TROTMAN), 94.
$C_{10}H_{14}O_2$ Camphorquinone, rotation of (LOWRY and CUTTER), 614.
β-Phenyl-β-methylpropane-$\alpha\gamma$-diol (MILLS and BAINS), 2503.
$C_{10}H_{14}O_4$ 2-Carboxy*bicyclo*-[4,1,0]heptane-1-acetic acid (BAKER), 989.
Δ^1-*cyclo*Hexene-1:2-diacetic acid (BAKER), 990.
$C_{10}H_{14}O_5$ Anhydro-β-methylpimelic-β-acetic acid (FARMER and ROSS), 2364.
1:2-Dihydroxy*cyclo*hexane-1:2-diacetolactone (BAKER), 989.
$C_{10}H_{14}N_2$ Nicotine, rotation of (PATTERSON and FULTON), 2439.
$C_{10}H_{15}Br$ β-Bromo-α-phenyl-β-methylbutane (TROTMAN), 91.
$C_{10}H_{15}As$ *p*-Tolylmethylethylarsine (MILLS and RAPER), 2481.
$C_{10}H_{16}O$ Camphor, rotation of (LOWRY and CUTTER), 612; rotation of halogen derivatives (CUTTER, BURGESS, and LOWRY), 1260.
Tagetone (JONES and SMITH), 2538.
$C_{10}H_{16}O_2$ Diethyldihydroresorcinol (KON and LINSTEAD), 819.
l-2:2:4-Trimethyl-Δ^3-*cyclo*hexene-1-carboxylic acid (GIBSON and SIMONSEN), 1303.
$C_{10}H_{16}O_5$ Ethyl acetylsuccinate, halogenation of (MACBETH and TRAILL), 1118.
$C_{10}H_{16}O_6$ β-Methylpimelic-β-acetic acid (FARMER and ROSS), 2364.
$C_{10}H_{16}N_2$ *cyclo*Pentylideneazine, action of hydrochloric acid on (PERKIN and PLANT), 1138.
$C_{10}H_{18}O$ Borneol, rotation of (LOWRY and CUTTER), 614.
$\gamma\eta$-Dimethyl-Δ^α-octen-ϵ-one (JONES and SMITH), 2534.
α- and β-Fenchyl alcohols, and their esters, rotatory powers of (KENYON and PRISTON), 1472.
Substance, from reduction of tagetone (JONES and SMITH), 2538.
$C_{10}H_{18}O_2$ *dl-sec.*-Amylacetylacetone, and its copper salt (MORGAN and ELVINS), 2623.
$C_{10}H_{18}O_4$ *iso*Propyl-*n*-butylmalonic acid (JONES and PYMAN), 2597.
$C_{10}H_{18}O_6$ Tetramethyl galactonolactone (PRYDE, HIRST, and HUMPHREYS), 352.
$C_{10}H_{18}O_7$ Methyl arabotrimethoxyglutarate (HIRST and ROBINSON), 362.
$C_{10}H_{20}O$ $\gamma\eta$-Dimethyl-$\Delta\alpha$-octen-ϵ-ol (JONES and SMITH), 2535.
$C_{10}H_{20}O_6$ Trimethyl methylglucoside (IRVINE and OLDHAM), 2920.
$C_{10}H_{21}N$ *l*-Menthylamine, aluminioxalate of (CHILD, ROBERTS, and TURNER), 2972.
$C_{10}H_{22}O$ $\gamma\eta$-Dimethyloctan-ϵ-ol (JONES and SMITH), 2535.

10 III

$C_{10}H_6O_2Cl_6$ Methyl 2:4-di(trichloromethyl)benzoate (PERKIN and STONE), 2296.
$C_{10}H_7OTl$ Thallous α-naphthoxide (CHRISTIE and MENZIES), 2373.
$C_{10}H_7O_3N$ 4-Cyanomethyl-1:2-phthalide (PERKIN and STONE), 2288.
$C_{10}H_7O_4N$ 2-Carboxy-4:5-methylenedioxyphenylacetonitrile (HAWORTH and PINK), 1370.
4:5-Methylenedioxyhomophthalimide (HAWORTH and PINK), 1371.

$C_{10}H_8O_2Cl_4$ Methyl 2:4-di(dichloromethyl)benzoate (PERKIN and STONE), 2291.
$C_{10}H_8O_3N_4$ Glyoxalinecarboxynitroanilides, and their salts (BALABAN and KING), 2705.
$C_{10}H_8O_4N_2$ β-6-Nitropiperonylpropionitrile (BAKER and ROBINSON), 1428.
$C_{10}H_8NBr$ 2-Bromo-6-methylquinoline, and its salts (CONOLLY), 2085.
$C_{10}H_9O_2N$ β-Piperonylpropionitrile (BAKER and ROBINSON), 1424.
$C_{10}H_9O_2N_3$ 2-*p*-Nitrophenyl-1-methylglyoxaline, and its salts (BALABAN and KING), 2710.
$C_{10}H_9O_3Li$ Lithium benzoylacetone ($+ 2H_2O$) (SIDGWICK and BREWER), 2383.
$C_{10}H_9O_3Na$ Sodium benzoylacetone ($+ 2H_2O$) (SIDGWICK and BREWER), 2383.
$C_{10}H_9O_3N$ Methoxyacetanthranils (HEILBRON, KITCHEN, PARKES, and SUTTON), 2173.
1:2-Phthalide-4-acetamide (PERKIN and STONE), 2288.
$C_{10}H_9O_4N$ Acetyl-3:4-methylenedioxy-α-benzaldoxime (BRADY and MCHUGH), 2422.
Methoxymethylisatoic anhydrides (HEILBRON, KITCHEN, PARKES, and SUTTON), 2174.
$C_{10}H_9O_4Br$ 6-Bromo-4:5-dimethoxyphthalide (RÂY and ROBINSON), 1622.
$C_{10}H_9O_5N$ 4:5-Methylenedioxyhomophthamic acid (HAWORTH and PINK), 1371.
$C_{10}H_9O_6N$ 6-Nitro-4:5-dimethoxyphthalide (RÂY and ROBINSON), 1621.
β-6-Nitropiperonylpropionic acid (BAKER and ROBINSON), 1428.
$C_{10}H_9O_7N$ 3-Nitro-4-ethylcarbonatobenzoic acid (KING and MURCH), 2649.
$C_{10}H_9N_2Br$ 5-Bromo-4-phenyl-1-methylglyoxaline, and its picrate (FORSYTH and PYMAN), 576.
1:4-Di-*p*-bromophenyl-3:6-diphenyl-1:4-dihydro-1:2:4:5-tetrazine (CHATTAWAY and WALKER), 982.
$C_{10}H_9N_4Br$ *p*-Bromobenzeneazomethylglyoxalines (BURTLES and PYMAN), 2016.
$C_{10}H_9Cl_2As$ Phenyl-ββ′-dichlorodivinylarsine (HUNT and TURNER), 997.
$C_{10}H_{10}ON_4$ Glyoxalinecarboxyaminoanilides, and their salts (BALABAN and PYMAN), 2706.
$C_{10}H_{10}O_2Br_2$ Methyl 2:4-di(bromomethyl)benzoate (PERKIN and STONE), 2287.
$C_{10}H_{10}O_4N_2$ Acetyl-3-nitro-4-methyl-α-benzaldoxime (BRADY, COSSON, and ROPER), 2432.
$C_{10}H_{10}O_8N_2$ Glycerol α-mono-3:5-dinitrobenzoate (FAIRBOURNE and FOSTER), 2763.
$C_{10}H_{10}N_2S$ 2-Thiol-1-phenyl-4-methylglyoxaline (BURTLES, PYMAN, and ROYLANCE), 589.
$C_{10}H_{11}ON$ 4-Ketomethyl-1:2:3:4-tetrahydroquinolines (CLEMO and PERKIN), 2303.
$C_{10}H_{11}O_2N$ 6-Methoxy-4-keto-1:2:3:4-tetrahydroquinoline (CLEMO and PERKIN), 2306.
$C_{10}H_{11}O_2Br$ Methyl bromodimethylbenzoates (PERKIN and STONE), 2285.
$C_{10}H_{11}O_4N$ 6-Amino-4:5-dimethoxyphthalide (RÂY and ROBINSON), 1622.
$C_{10}H_{11}O_5N$ 5-Nitro-4-methoxy-2-ethoxybenzaldehyde (RAO, SRIKANTIA, and IYENGAR), 559.
6-Nitro-3-methoxy-2-ethoxybenzaldehyde (RUBENSTEIN), 2269.
$C_{10}H_{11}O_6N$ 6-Nitro-3-methoxy-2-ethoxybenzoic acid (RUBENSTEIN), 2269.
$C_{10}H_{12}O_2N_2$ Malonmonomethylmonophenylamide (WEST), 750.
$C_{10}H_{12}O_3N_2$ Acetonitrobenzylmethylamides (HOLMES and INGOLD), 1818.
$C_{10}H_{12}O_5N_2$ 4-Nitro-2:5-dimethoxyacetanilide (RUBENSTEIN), 2003.
$C_{10}H_{12}O_5S$ *d*-α-*p*-Toluenesulphonoxypropionic acid, rotatory power and reactions of (KENYON, PHILLIPS, and TURLEY), 412.
$C_{10}H_{13}ON$ Acetomethylbenzylamide (HOLMES and INGOLD), 1818.
$C_{10}H_{13}OCl$ α-Chloro-γ-hydroxy-β-phenyl-β-methylpropane (MILLS and BAINS), 2504.

$C_{10}H_{13}OBr$ α-Bromo-γ-hydroxy-β-phenyl-β-methylpropane (MILLS and BAINS), 2504.

$C_{10}H_{13}O_2N$ γ-Piperonylpropylamine, and its hydrochloride (BAKER and ROBINSON), 1428.

$C_{10}H_{13}O_2Br$ β-Bromocamphorquinone (BURGESS and LOWRY), 277.

$C_{10}H_{13}O_2N_3$ δ-3-Carbethoxyphenylsemicarbazide, and its hydrochloride (WILSON and CRAWFORD), 107.

$C_{10}H_{15}O_2Br$ Ethyl 2-bromo-Δ^1-*cyclo*hexeneacetate (BAKER), 988.

$C_{10}H_{15}O_5Cl$ Ethyl α-chloroacetylsuccinate (MACBETH and TRAILL), 1120.

$C_{10}H_{16}O_2Br_2$ Ethyl 1:2-dibromo*cyclo*hexane-1-acetate (BAKER), 988.

$C_{10}H_{16}O_2Te$ 4-*sec.*-Amyl*cyclo*telluropentane-3:5-dione (MORGAN and ELVINS), 2624.

$C_{10}H_{17}ON$ Tagetone oxime (JONES and SMITH), 2538.

$C_{10}H_{17}ON_3$ α-Methyl-Δ^1-*cyclo*pentenylacetone semicarbazone (KON and LINSTEAD), 821.

$C_{10}H_{17}O_3N$ *d*-2:2:4-Trimethyl*cyclo*hexan-3-one-1-carboxylic acid oxime (GIBSON and SIMONSEN), 1298.

$C_{10}H_{17}O_3N_3$ 1-Methyl*cyclo*hexan-3-one-1-acetic acid semicarbazone (FARMER and ROSS), 2365.

$C_{10}H_{17}O_4Cl$ Ethyl γ-chloro-α-methylglutarate (INGOLD), 394.

$C_{10}H_{17}O_4Br$ Ethyl γ-bromo-α-methylglutarate (INGOLD), 393.

$C_{10}H_{17}O_4I$ Ethyl α-iodo-α-methylglutarate (INGOLD), 394.

$C_{10}H_{19}ON$ γη-Dimethyl-Δ^α-octen-ε-one oxime (JONES and SMITH), 2535.

n- and *iso*-Menthoneoximes (READ and COOK), 2786.

$C_{10}H_{19}O_3N_3$ β-*iso*Valeryl-α-methylpropionic acid semicarbazone (JONES and SMITH), 2536.

$C_{10}H_{19}O_8N$ Trimethyl methylglucoside 6-mononitrate (OLDHAM), 2841.

$C_{10}H_{20}O_6S_2$ Menthanedisulphonic acid, barium salt (KOLKER and LAPWORTH), 314.

$C_{10}H_{21}ON$ γη-Dimethyloctan-ε-one oxime (JONES and SMITH), 2535.

$C_{10}H_{21}O_6N$ Tetramethyl galactonamide (PRYDE, HIRST, and HUMPHREYS), 353.

10 IV

$C_{10}H_7O_2IS$ Naphthalene-2-sulphonyl iodide (GIBSON, MILLER, and SMILES), 1823.

$C_{10}H_9O_5BrS$ 4-Bromo-2-carboxy-5-methoxyphenylthiolacetic acid (GRIFFITH and HOPE), 994.

$C_{10}H_9O_6N_4As$ Glyoxalinecarboxy-*p*-amino-3-nitrophenylarsinic acid, $(+H_2O)$ and its salts (BALABAN and KING), 2708.

$C_{10}H_{10}O_2N_2Br_2$ Bromomalonmonomethylmono-*p*-bromophenylamide (WEST), 751.

$C_{10}H_{10}O_4NBr$ 5-Bromo-2-acetylamino-4-methoxybenzoic acid (GRIFFITH and HOPE), 993.

$C_{10}H_{10}O_4N_3As$ Glyoxalinecarboxy-*p*-aminophenylarsinic acid, $(+H_2O)$ and its salts (BALABAN and KING), 2708.

$C_{10}H_{11}OCl_3Te$ Tellurium phenyl-*n*-propylketone trichloride (MORGAN and ELVINS), 2631.

$C_{10}H_{11}O_2N_2Br$ Bromomalonmono-*p*-tolylamide (WEST), 752.

$C_{10}H_{11}O_4N_4As$ Glyoxalinecarboxy-*p*-amino-3-aminophenylarsinic acid, $(+\frac{1}{2}H_2O)$ and its salts (BALABAN and KING), 2709.

$C_{10}H_{12}O_2NCl$ 5-Chloro-2-acetylamino-4-methoxytoluene (HEILBRON, KITCHEN, PARKES, and SUTTON), 2175.

$C_{10}H_{12}O_2NBr$ 5-Bromo-2-acetylamino-*p*-tolyl methyl ether (GRIFFITH and HOPE), 992.

$C_{10}H_{12}O_3NBr$ 4-Bromo-2:5-dimethoxyacetanilide (RUBENSTEIN), 2003.

$C_{10}H_{12}O_6NAs$ 3-Acetylamino-4-acetoxyphenylarsinic acid (King and Murch), 2651.

$C_{10}H_{13}ONS$ *iso*Propyl phenylthiocarbamate (Birch and Norris), 904.

$C_{10}H_{13}O_2NS$ *iso*Propyl mercaptan *p*-nitrobenzyl ether (Birch and Norris), 904.

$C_{10}H_{13}O_2SAs$ *p*-Carboxyphenylmethylethylarsine sulphides, and their salts (Mills and Raper), 2481.

$C_{10}H_{13}O_4NS$ *d*-α-*p*-Toluenesulphonoxypropionamide (Kenyon, Phillips, and Turley), 412.

$C_{10}H_{15}O_4SBr$ β-Bromocamphor-α-sulphonic acid, and its salts (Burgess and Lowry), 271.

$C_{10}H_{16}O_2Cl_2Te$ 4-*sec.*-Amyl*cyclo*telluripentane-3:5-dione dichloride (Morgan and Elvins), 2624.

$C_{10}H_{12}O_2Cl_2Te$ Tellurium bismethylpropylketone dichlorides (Morgan and Elvins), 2628.

10 V

$C_{10}H_{12}O_2ClBrS$ α-Bromocamphor-π-chlorosulphoxide (Burgess and Lowry), 282.

$C_{10}H_{14}O_3ClBrS$ β-Bromocamphor-α-sulphonyl chloride (Burgess and Lowry), 271.

$C_{10}H_{15}O_3NBr_2S$ α′β-Dibromocamphor-α-sulphonamide (Burgess and Lowry), 277.

$C_{10}H_{16}O_3NBrS$ β-Bromocamphor-α-sulphonamide (Burgess and Lowry), 275.

$C_{10}H_{18}O_4NBrS$ Acetyl-β-bromocamphor-α-sulphonamide (Burgess and Lowry), 276.

C_{11} Group.

$C_{11}H_8O_5$ Piperonylsuccinic anhydride (Baker and Lapworth), 566.

$C_{11}H_{10}O_4$ 7-Acetoxy-3:4-dihydrocoumarin (Chapman and Stephen), 890.

Anisylsuccinic anhydride (Baker and Lapworth), 566.

$C_{11}H_{10}O_5$ 3-Methoxy-5:7-dihydroxy-2-methylchromone (Kalff and Robinson), 1972.

$C_{11}H_{12}O_2$ 2-Hydroxystyryl ethyl ketone (McGookin and Sinclair), 2542.

$C_{11}H_{12}O_5$ Anisylsuccinic acid (Baker and Lapworth), 565.

$C_{11}H_{12}O_6$ Vanillylsuccinic acid (Baker and Lapworth), 564.

$C_{11}H_{14}O_6$ Δ^1-*cyclo*Hexene-1-acetic-2-malonic acid (Baker), 988.

$C_{11}H_{16}O_2$ β-Phenyl-γ-methylbutylene βγ-glycol, synthesis of (Roger), 522.

$C_{11}H_{16}O_4$ 2:3-Dimethoxybenzaldehyde dimethylacetal (Haworth and Perkin), 1437.

Acetyl derivative of lactone $C_9H_{14}O_3$ (Goodson and Henry), 1648.

$C_{11}H_{18}O_2$ Methyl *l*-2:2:4-trimethyl-Δ^3-*cyclo*hexene-1-carboxylate (Gibson and Simonsen), 1302.

$C_{11}H_{18}O_3$ Ethyl 1-methyl*cyclo*hexan-3-one-1-acetate (Farmer and Ross), 2365.

$C_{11}H_{18}O_3$ Methyl *d*-2:2:4-trimethyl*cyclo*hexan-3-one-1-carboxylate (Gibson and Simonsen), 1299.

$C_{11}H_{18}O_5$ Ethyl α-keto-ββ-dimethylglutarate (Rothstein, Stevenson, and Thorpe), 1079.

$C_{11}H_{18}O_6$ αα′-Dihydroxy*cyclo*heptane-1:1-diacetic acid, and its silver salt (Baker), 1681.

$C_{11}H_{18}N_2$ *cyclo*Hexylidene*cyclo*pentylideneazine (Perkin and Plant), 1141.

$C_{11}H_{20}O_2$ *n*-Octoylacetone, and its copper salt (Morgan and Holmes), 2892.

$C_{11}H_{20}O_3$ Methyl *trans*-*d*-3-hydroxy-2:2:4-trimethyl*cyclo*hexane-1-carboxylate (Gibson and Simonsen), 1302.

Ethyl *iso*valeryl-α-methylpropionate (Jones and Smith), 2536.

11 III

$C_{11}H_9O_3N$ α-Carbethoxy-γ-hydroxy-γ-phenyl-Δβ-propenecarboxylamide (R. M. and J. N. RÂY), 2722.

$C_{11}H_{10}O_4Br_2$ αα′-Dibromo-β-phenylglutaric acid (HAERDI and THORPE), 1242.

$C_{11}H_{11}ON$ 4-Methoxy-6-methylquinoline (CLEMO and PERKIN), 2305.

$C_{11}H_{11}O_2N_3$ 3-*iso*Propylideneaminotetrahydroquinazoline-2:4-dione (WILSON and CRAWFORD), 109.

$C_{11}H_{11}O_4N$ 2-Carboxy-4:5-dimethoxyphenylacetonitrile (HAWORTH and PINK), 1370.

4:5-Dimethoxyhomophthalimide (HAWORTH and PINK), 1370.

$C_{11}H_{11}O_4Br$ *o*-Bromobenzylidene diacetate (BRADY, COSSON, and ROPER), 2429.

$C_{11}H_{11}N_4Br$ 2-*p*-Bromobenzeneazo-4:5-dimethylglyoxaline, and its hydrochloride (BURTLES and PYMAN), 2014.

$C_{11}H_{12}O_2N_2$ Methoxydimethyl-4-quinazolones (HEILBRON, KITCHEN, PARKES, and SUTTON), 2173.

$C_{11}H_{12}O_5N_2$ Succin-2-nitro-*p*-toluidic acid (BRADY, QUICK, and WELLING), 2267.

$C_{11}H_{12}O_7N_2$ Acetyl derivative of trimethylene glycol monodinitrophenyl ether (FAIRBOURNE and FOSTER), 2762.

$C_{11}H_{12}N_2S$ 2-Ethylthiol-1-phenylglyoxaline, picrate of (BURTLES, PYMAN, and ROYLANCE), 590.

$C_{11}H_{13}ON_3$ *p*-Tolueneazoallylformaldoxime (WALKER), 1862.

$C_{11}H_{13}O_2N$ Diacetylbenzylamine (HOLMES and INGOLD), 1820.

6-Ethoxy-4-keto-1:2:3:4-tetrahydroquinoline (CLEMO and PERKIN), 2306.

β-Veratrylpropionitrile (BAKER and ROBINSON), 1433.

$C_{11}H_{13}O_3N$ Acetyl-4-methoxy-3-methyl-α-benzaldoxime (BRADY, COSSON, and ROPER), 2431.

$C_{11}H_{13}O_4N$ Carbethoxymethylanthranilic acid (HEILBRON, KITCHEN, PARKES, and SUTTON), 2171.

5-Nitro-4-allylveratrole (LIONS, PERKIN, and ROBINSON), 1167.

$C_{11}H_{13}O_5N$ 4:5-Dimethoxyhomophthalamic acid (HAWORTH and PINK), 1370.

Nitro-2:3-diethoxybenzaldehydes (RUBENSTEIN), 2269.

$C_{11}H_{13}O_6N$ Methyl 2-cyano*cyclo*butane-1:2:3-tricarboxylate (ING and PERKIN), 2396.

$C_{11}H_{15}O_2N$ 6:7-Dimethoxy-1:2:3:4-tetrahydro*iso*quinoline, and its hydrochloride (FORSYTH, KELLY, and PYMAN), 1666.

$C_{11}H_{14}O_2N_2$ Malonmonoethylmonophenylamide (WEST), 750.

Malonmonomethylmono-*p*-tolylamide (WEST), 751.

$C_{11}H_{15}O_{10}N$ Acetonitropentose (OLDHAM), 2845.

$C_{11}H_{16}O_2N_2$ *neo*Pilocarpines, and their salts (BURTLES, PYMAN, and ROYLANCE), 584.

$C_{11}H_{17}ON_3$ Base, and its salts, from chenopodium oil (HENRY and PAGET), 1656.

$C_{11}H_{17}O_4N$ Ethyl *as*-dimethylcyanosuccinate, preparation and stability of (INGOLD), 472.

$C_{11}H_{18}O_2Te$ 2-*n*-Hexyl*cyclo*telluropentane-3:5-dione (MORGAN and TAYLOR), 805.

$C_{11}H_{19}ON_3$ α-Ethyl-Δ^1-*cyclo*pentenylacetone semicarbazone (KON and LINSTEAD), 821.

$C_{11}H_{19}O_3N$ Methyl *d*-2:2:4-trimethyl*cyclo*hexan-3-one-1-carboxylate oxime (GIBSON and SIMONSEN), 1299.

$C_{11}H_{21}ON_3$ γη-Dimethyl-Δα-octen-ε-one semicarbazone (JONES and SMITH), 2535.

dl-Menthonesemicarbazones (READ and COOK), 2787.

$C_{11}H_{23}ON_3$ γη-Dimethyloctan-ε-one semicarbazone (JONES and SMITH), 2535.

δ-Menthylsemicarbazide, and its hydrochloride (WILSON and CRAWFORD), 106.

11 IV

$C_{11}H_9ONS$ α-Thiocyanostyryl methyl ketone (CHALLENGER and BOTT), 1040.

$C_{11}H_{10}O_3NI_3$ Thyroxin, relation of, to tryptophan (HICKS), 771.

$C_{11}H_{12}O_2N_2Br_2$ Bromomalonmonoethylmono-*p*-bromophenylamide (WEST), 751.

$C_{11}H_{13}ONS$ Substance, from carvone and thiocyanogen (CHALLENGER and BOTT), 1041.

$C_{11}H_{13}O_2N_2Br$ Bromomalonmonomethylmono-*p*-tolylamide (WEST), 751.

$C_{11}H_{14}ON_2S$ 2-Anilino-5-ethoxy-4:5-dihydrothiazole (BURTLES, PYMAN, and ROYLANCE), 590.

$C_{11}H_{15}ONS$ *iso*Butyl phenylthiocarbamate (BIRCH and NORRIS), 905.

$C_{11}H_{18}O_2Cl_2Te$ 2-*n*-Hexyl*cyclo*telluripentane-3:5-dione 1:1-dichloride (MORGAN and TAYLOR), 804.

$C_{11}H_{20}O_2NBr$ 4-Carboxybispiperidinium-1:1′-spiran bromide, and its picrate (MILLS and BAINS), 2506.

11 V

$C_{11}H_9ONBr_2S$ α-Thiocyanostyryl methyl ketone dibromide (CHALLENGER and BOTT), 1041.

C_{12} Group.

$C_{12}H_{10}O_6$ Carboxyphenylparaconic acid (HAERDI and THORPE), 1246.

$C_{12}H_{10}N_2$ 3-Methyl-3-*iso*carboline (ARMIT and ROBINSON), 1612.

$C_{12}H_{14}O_2$ 3-Benzylacetylacetone, and its salts (MORGAN and TAYLOR), 801.

2-Hydroxystyryl *n*-propyl ketone (MCGOOKIN and SINCLAIR), 2542.

β-Phenylpropionylacetone, copper salt (MORGAN and JONES), 2619.

$C_{12}H_{14}O_3$ 3-Methoxy-4-hydroxystyryl ethyl ketone (MCGOOKIN and SINCLAIR), 2543.

$C_{12}H_{14}N_2$ 1-Anilino-1-cyano*cyclo*pentane (PLANT and FACER), 2038.

$C_{12}H_{16}O_4$ Benzoyl dimethyl glycerol (GILCHRIST and PURVES), 2743.

Ethyl ethane-$^{1:2}$Π$^{1:4}$-1-methyl*cyclo*hexa-3:5-dione-2-carboxylate (FARMER and ROSS), 2366.

$C_{12}H_{16}O_5$ ω:3:4:5-Tetramethoxyacetophenone (PRATT and ROBINSON), 173.

$C_{12}H_{16}O_8$ Dextrin triacetate (IRVINE and OLDHAM), 2915.

Methyl *cyclo*butane-1:2:2:3-tetracarboxylate (ING and PERKIN), 2395.

$C_{12}H_{18}O_5$ Ethyl hydrogen 1-methyl*cyclo*hexan-3-one-4-carboxylate-3-acetate (FARMER and ROSS), 2366.

*cyclo*Heptane*spiro*-1-methoxy*cyclo*propane-1:2-dicarboxylic acid (BAKER), 1680.

$C_{12}H_{20}O_5$ Ethyl methoxycaronate (ROTHSTEIN, STEVENSON, and THORPE), 1079.

$C_{12}H_{20}O_6$ Tetramethylglucose, mutarotation of, in various solvents (LOWRY and RICHARDS), 1385.

$C_{12}H_{20}N_2$ *cyclo*Hexylideneazine, action of hydrochloric acid on (PERKIN and PLANT), 1138.

$C_{12}H_{21}O_4$ 3-*sec.*-Amyldipropionylmethane (MORGAN and ELVINS), 2624.

$C_{12}H_{22}O_2$ *n*-Nonoylacetone, and its copper salt (MORGAN and HOLMES), 2893.

$C_{12}H_{22}O_3$ *l*-Menthyl glycollate (RULE and SMITH), 2191.

$C_{12}H_{22}O_5$ Diethyl α-keto-ββ-dimethylpentane-αγ-dicarboxylate (ROTHSTEIN, STEVENSON, and THORPE), 1077.

Ethyl ester of acid, $C_8H_{14}O_5$ (GOSS and INGOLD), 2779.

$C_{12}H_{22}O_6$ Ethyl phenyl*cyclo*propanetricarboxylate (HAERDI and THORPE), 1246.

$C_{12}H_{24}O_2$ Lauric acid, potassium salt, effect of potassium chloride on solutions of (QUICK), 1401.

12 III

$C_{12}H_8ClAs$ *oo′*-Diphenylylenearsenious chloride (AESCHLIMANN, LEES, MCCLELAND, and NICKLIN), 68.

$C_{12}H_6Cl_3As$ Di-*p*-chlorophenylchloroarsine (HUNT and TURNER), 2671.

$C_{12}H_9O_2As$ *oo'*-Diphenylylenearsinic acid (AESCHLIMANN, LEES, MCCLELAND, and NICKLIN), 68.

$C_{12}H_9O_3As$ Diphenylyl-*o*-arsinic acid (AESCHLIMANN, LEES, MCCLELAND, and NICKLIN), 68.

$C_{12}H_{10}O_2Se$ α-Naphthylselenoglycollic acid (MORGAN and PORRITT), 1758.

$C_{12}H_{10}N_2S_2$ 4:4'-Diaminodiphenyl trisulphide, and its hydrochloride (HODGSON and WILSON), 443.

$C_{12}H_{11}O_4N$ α-Cyano-β-veratrylacrylic acid (BAKER and ROBINSON), 1432.

$C_{12}H_{11}O_2Br$ Methyl hydrogen 1-bromo-3-phenyl*cyclo*propane-1:2-dicarboxylate (HAERDI and THORPE), 1244.

$C_{12}H_{11}O_4As$ *o*-Phenoxyphenylarsinic acid (TURNER and SHEPPARD), 546.

$C_{12}H_{11}O_5N_3$ Pyridine 3:5-dinitro-*o*-tolyl oxide (GIBSON), 45.

$C_{12}H_{12}O_2N_2$ Ethyl 4(5)-phenylglyoxaline-5(4)-carboxylate (FORSYTH and PYMAN), 580.

Methyl 3-amino-2-methylcinchoninate (GULLAND and ROBINSON), 1497.

$C_{12}H_{12}O_2Te$ 2-Benzyl*cyclo*telluropentane-3:5-dione (MORGAN and JONES), 2620.

4-Benzyl*cyclo*telluropentane-3:5-dione (MORGAN and TAYLOR), 801.

$C_{12}H_{12}O_3N_2$ 6:7-Dimethoxy*iso*quinoline-1-carboxylamide (HAWORTH and PERKIN), 1442.

$C_{12}H_{13}ON$ ψ-Indoxyl*spirocyclo*pentane, alkali salts of (SIDGWICK and PLANT), 209.

$C_{12}H_{13}O_3N$ Carbethoxy-α-cinnamaldoxime (BRADY and MCHUGH), 2426.

$C_{12}H_{13}O_4N$ α-Cyano-β-veratrylpropionic acid (BAKER and ROBINSON), 1433.

$C_{12}H_{14}O_3N_2$ 1-Anilino*cyclo*pentane-1-carboxynitrosoamine (PLANT and FACER), 2039.

$C_{12}H_{15}O_2N$ 1-Anilino*cyclo*pentane-1-carboxylic acid (PLANT and FACER), 2039.

$C_{12}H_{15}O_3N_3$ Nitrosoamine of 1-anilino*cyclo*pentane-1-carboxylamide (PLANT and FACER), 2039.

$C_{12}H_{15}O_2Br$ α-Bromo-γ-acetoxy-β-phenyl-β-methylpropane (MILLS and BAINS), 2505.

$C_{12}H_{15}O_3N$ Acetylpiperonylpropylamine (BAKER and ROBINSON), 1429.

$C_{12}H_{16}ON_2$ 1-Anilino*cyclo*pentane-1-carboxylamide (PLANT and FACER), 2039.

$C_{12}H_{16}O_2N_2$ Malonmonoethylmono-*p*-tolylamide (WEST), 751.

$C_{12}H_{17}O_2Br$ Bromoacetoxydihydro-*p*-cymene (HENRY and PAGET), 1658.

$C_{12}H_{18}O_2N_2$ Ethylenediaminobisacetylacetone, diaquocobalt salt (MORGAN and SMITH), 2034.

$C_{12}H_{15}O_3N_2$ Diphenylcarbamyl-ɔ-methoxy-β-benzaldoxime (BRADY and MCHUGH), 2426.

$C_{12}H_{20}O_2Te$ 2-*n*-Heptyl*cyclo*telluropentane-3:5-dione (MORGAN and TAYLOR), 805.

$C_{12}H_{21}O_3N_3$ Ethyl 1-methyl*cyclo*hexan-3-one-1-acetate semicarbazone (FARMER and ROSS), 2365.

Methyl *d*-2:2:4-trimethyl*cyclo*hexan-3-one-1-carboxylate semicarbazones (GIBSON and SIMONSEN), 1300.

$C_{12}H_{22}O_2N$ *N*-Methylol-Δ$^{\omega}$-undecenoamide (JONES and PYMAN), 2598.

12 IV

$C_{12}H_7OCl_2As$ Dichlorophenoxarsines (ROBERTS and TURNER), 2010.

$C_{12}H_8OClAs$ 6-Chlorophenoxarsine (TURNER and SHEPPARD), 544.

$C_{12}H_8OCl_3As$ Chlorophenoxyphenyldichloroarsines (ROBERTS and TURNER), 2009.

$C_{12}H_8O_3NCl$ Chloronitrodiphenyl ethers (ROBERTS and TURNER), 2008.

$C_{12}H_8O_2ClAs$ Chlorophenoxarsinic acids (ROBERTS and TURNER), 2010.

$C_{12}H_{10}ONCl$ Chloroaminodiphenyl ethers, and their hydrochlorides (ROBERTS and TURNER), 2008.

$C_{12}H_{10}O_4ClAs$ Chlorophenoxyphenylarsinic acids (ROBERTS and TURNER), 2009.

$C_{12}H_{12}O_2N_2S$ Ethyl 2-thiol-4(5)-phenylglyoxaline-5(4)-carboxylate (FORSYTH and PYMAN), 579.

$C_{12}H_{12}O_2Cl_2Te$ 4-Benzyl*cyclo*telluripentane-3:5-dione 1:1-dichloride (MORGAN and TAYLOR), 801.

$C_{12}H_{14}O_2NI$ 6:7-Dimethoxy*iso*quinoline methiodide (FORSYTH, KELLY, and PYMAN), 1666.

$C_{12}H_{14}O_2N_2Te$ 4-Benzyl*cyclo*telluropentane-3:5-dionedioxime (MORGAN and TAYLOR), 801.

$C_{12}H_{15}O_2N_2Br$ Bromomalonmonoethylmono-*p*-tolylamide (WEST), 751.

$C_{12}H_{16}ON_2S$ 2-Anilino-5-ethoxy-4-methyl-4:5-dihydrothiazole, picrate of (BURTLES, PYMAN, and ROYLANCE), 589.

$C_{12}H_{20}O_2Cl_2Te$ 2-*n*-Heptyl*cyclo*telluripentane-3:5-dione 1:1-dichloride (MORGAN and TAYLOR), 805.

$C_{12}H_{21}O_2Cl_3Te$ Tellurium *n*-nonylacetone trichloride (MORGAN and TAYLOR), 806.

$C_{12}H_{22}O_2Cl_2Te$ Tellurium bismethylbutylketone dichlorides (MORGAN and ELVINS), 2629.

Tellurium bispinacolin dichloride (MORGAN and ELVINS), 2630.

$C_{12}H_{29}O_5N_4Co$ Diamminoethylene diaminobisacetonecobaltic hydroxide, salts of (MORGAN and SMITH), 2034.

$C_{12}H_{36}Cl_2Sb_4Pd$ Tetrakistrimethylstibinepalladous chloride (MORGAN and YARSLEY), 190.

12 V

$C_{12}H_6O_2Cl_2Br_2S_2$ 2:5-Dibromophenyl 2:5-dichlorobenzenethiolsulphonate (MILLER and SMILES), 230.

2:5-Dichlorophenyl 2:5-dibromobenzenethiolsulphonate (MILLER and SMILES), 230.

$C_{12}H_7O_4NCl_2S_2$ 2:5-Dichlorophenyl 2-nitrobenzenethiolsulphonate (MILLER and SMILES), 230.

2-Nitrophenyl 2:5-dichlorobenzenethiolsulphonate (MILLER and SMILES), 229.

$C_{12}H_8O_4NClS_2$ 2-Nitrophenyl 4-chlorobenzenethiolsulphonate (MILLER and SMILES), 229.

$C_{12}H_{36}Cl_4SbPtPd$ Tetrakistrimethylstibineplatinous palladochloride (MORGAN and YARSLEY), 189.

C_{13} Group.

$C_{13}H_{11}As$ Diphenylylenemethylarsine (AESCHLIMANN, LEES, MCCLELAND, and NICKLIN), 69.

$C_{13}H_{12}O_6$ Acetovanillylsuccinic anhydride (BAKER and LAPWORTH), 505.

α-Carbethoxy-γ-hydroxy-γ-phenyl-Δβ-propenecarboxylactone (R. M. and J. N. RÂY), 2722.

Ethyl 4-hydroxymethyl-1:2-phthalideoxalate (PERKIN and STONE), 2287.

$C_{13}H_{12}O_7$ 2:4:6-Triacetoxybenzaldehyde ($+\frac{1}{2}H_2O$) (PRATT and ROBINSON), 1184.

$C_{13}H_{13}N$ Benzylaniline, reactions of antimony halides with (VANSTONE), 552.

$C_{13}H_{14}O_5$ 2-Ethoxy-3-phenyl*cyclo*propane-1:2-dicarboxylic acid, and its silver salt (HAERDI and THORPE), 1242.

$C_{13}H_{16}O_2$ 3-Benzylpropionylacetone, and its copper salt (MORGAN and CORBY), 2618.

$C_{13}H_{18}O_3$ 3-Methoxy-4-hydroxystyryl *n*-propyl ketone (MCGOOKIN and SINCLAIR), 2543.

$C_{13}H_{20}O_2$ β-Phenyl-γ-ethylamylene βγ-glycol (ROGER), 523.

$C_{13}H_{20}O_6$ γδ-Dicarbethoxy-γ-hydroxy-ββ-dimethylbutane-α-carboxylactone (ROTHSTEIN, STEVENSON, and THORPE), 1080.

$C_{13}H_{20}O_9$ Triacetyl methylglucoside (OLDHAM), 2844.
$C_{13}H_{22}O_4$ *l*-Menthyl hydrogen malonate (RULE and SMITH), 2192.
$C_{13}H_{22}O_6$ Ethyl *as*-dimethylcarboxysuccinate (INGOLD), 473.
$C_{13}H_{24}O_3$ *l*-Menthyl methoxyacetate (RULE and SMITH), 2191.
$C_{13}H_{24}O_6$ Ethyl $\beta\beta'$-dimethoxydiethylmalonate (BENNETT), 1279.

13 III

$C_{13}H_7O_9N_5$ Picrylnitrobenz*syn*aldoximes (BRADY and KLEIN), 846.
$C_{13}H_8O_7N_4$ Picrylbenz*syn*aldoxime (BRADY and KLEIN), 846.
$C_{13}H_8N_2Cl_4$ Benzaldehydetetrachlorophenylhydrazone (HUMPHRIES, HUMBLE, and EVANS), 1307.
$C_{13}H_8NAs$ *oo'*-Diphenylylenearsenious cyanide (AESCHLIMANN, LEES, MCCLELAND, and NICKLIN), 69.
$C_{13}H_9N_2Cl_3$ Benzaldehyde-*p*-chlorophenylhydrazone (HUMPHRIES, HUMBLE, and EVANS), 1306.
Chlorobenzaldehyde-2:4-dichlorophenylhydrazones (HUMPHRIES, HUMBLE, and EVANS), 1307.
$C_{13}H_9N_2Br_3$ Bromobenzaldehyde-2:4-dibromophenylhydrazones (CHATTAWAY and WALKER), 980.
$C_{13}H_{10}O_2N_2$ Anhydro-3-acetylamino-2-methylcinchoninic acid (GULLAND and ROBINSON), 1498.
$C_{13}H_{10}O_4N_2$ *m*-Nitrophenyl phenylcarbamate (BRADY and HARRIS), 2175.
$C_{13}H_{10}O_5N_4$ Nitrohydroxybenzaldehyde-*p*-nitrophenylhydrazones (HODGSON and BEARD), 880.
$C_{13}H_{11}ON$ Benzanilide, reactions of antimony halides with (VANSTONE), 550.
$C_{13}H_{11}O_2N$ Phenyl*cyclo*iminotoluquinone (CHATTAWAY and PARKES), 1310.
$C_{13}H_{11}O_2N_3$ Phenylaziminotoluquinone (CHATTAWAY and PARKES), 1309.
$C_{13}H_{11}N_2Br_2$ Benzaldehyde-2:4-dibromophenylhydrazidine (CHATTAWAY and WALKER), 981.
$C_{13}H_{12}O_2N_2$ 3-Acetylamino-2-methylcinchoninic acid (GULLAND and ROBINSON), 1497.
$C_{13}H_{12}BrAs$ *p*-Bromodiphenylmethylarsine (HUNT and TURNER), 2670.
$C_{13}H_{13}ON_3$ 3-*p*-Hydroxybenzeneazo-2:6-lutidine, and its hydrochloride (GULLAND and ROBINSON), 1495.
$C_{13}H_{13}O_4Br$ Methyl 1-bromo-3-phenyl*cyclo*propane-1:2-dicarboxylate (HAERDI and THORPE), 1244.
Lactone of ethyl α-bromo-α'-hydroxy-β-phenylglutarate (HAERDI and THORPE), 1241.
$C_{13}H_{14}ON_4$ 2:4:2':4'-Tetra-aminobenzophenone (GULLAND and ROBINSON), 1499.
$C_{13}H_{14}O_2Te$ 4-Benzyl-2-methyl*cyclo*telluropentane-3:5-dione (MORGAN and CORBY), 2618.
$C_{13}H_{14}O_8N_2$ *iso*Propylidene glycerol 3:5-dinitrobenzoate (FAIRBOURNE and FOSTER), 2763.
$C_{13}H_{14}O_4Br_2$ Methyl $\alpha\alpha'$-dibromo-β-phenylglutarate (HAERDI and THORPE), 1241.
$C_{13}H_{15}O_2N$ Dimethoxy-2:4-dimethylquinolines, and their salts (LIONS, PERKIN, and ROBINSON), 1162.
$C_{21}H_{15}O_2N_3$ 3-Diphenylmethyleneaminotetrahydroquinazoline-2:4-dione (WILSON and CRAWFORD), 108.
$C_{13}H_{15}O_4N$ δ-*o*-Formylaminobenzoylvaleric acid (PATERSON and PLANT), 1798.
$C_{13}H_{15}O_4Br$ Methyl α-bromo-β-phenylglutarate (HAERDI and THORPE), 1241.
$C_{13}H_{17}ON$ Methylpentenoic acid *p*-toluidides (KON and LINSTEAD), 623.
$C_{13}H_{17}O_3N$ 5-Acetylamino-4-allylveratrole (LIONS, PERKIN, and ROBINSON), 1168.
β Dimethoxyanilinopropenyl methyl ketones (LIONS, PERKIN, and ROBINSON), 1162.

$C_{13}H_{17}O_3N_3$ Acetone-δ-carbethoxyphenylsemicarbazones (WILSON and CRAWFORD), 108.

$C_{13}H_{18}O_2N_2$ Malonmono*iso*propylmono-*p*-tolylamide (WEST), 751.

$C_{13}H_{18}O_3N_2$ Anhydrocotarninemethylamine, and its salts (HAWORTH and PERKIN), 1444.

$C_{13}H_{19}O_2N$ Dimethoxy-2:4-dimethyl-1:2:3:4-tetrahydroquinolines, and their salts (LIONS, PERKIN, and ROBINSON), 1162.

$C_{13}H_{19}O_8I$ Triacetyl methylglucoside 6-iodohydrin (OLDHAM), 2844.

$C_{13}H_{19}O_{11}N$ Triacetyl methylglucoside 6-nitrate (OLDHAM), 2843.

13 IV

$C_{13}H_6O_3N_3Cl_3$ 1-Trichlorophenyl-3-*o*-nitrophenyl*iso*diazomethanes (CHATTAWAY and WALKER), 2412.

$C_{13}H_7O_2N_3Cl_2$ 1-2:4-Dichlorophenyl-3-*o*-nitrophenyl*iso*diazomethane (CHATTAWAY and WALKER), 2412.

$C_{13}H_7O_3N_3Cl_4$ ω-Chloronitrobenzaldehydetrichlorophenylhydrazones (CHATTAWAY and WALKER), 1690, 2413.

$C_{13}H_7O_2N_3Br_2$ 1-2:4-Dibromophenyl-3-*o*-nitrophenyl*iso*diazomethane (CHATTAWAY and WALKER), 2411.

$C_{13}H_7O_2N_3Br_4$ ω-Bromo-*m*-nitrobenzaldehydetribromophenylhydrazone (CHATTAWAY and WALKER), 1695.

$C_{13}H_8O_2NBr_3$ 2:4:6-Tribromophenyl*cyclo*iminotoluquinone (CHATTAWAY and PARKES), 1311.

$C_{13}H_8O_2N_3Cl$ 1-*p*-Chlorophenyl-3-*o*-nitrophenyl*iso*diazomethane (CHATTAWAY and WALKER), 2412.

$C_{13}H_8O_3N_3Cl_3$ ω-Chloronitrobenzaldehydedichlorophenylhydrazones (CHATTAWAY and WALKER), 1691, 2413.

$C_{13}H_8O_2N_3Br$ 1-*p*-Bromophenyl-3-*o*-nitrophenyl*iso*diazomethane (CHATTAWAY and WALKER), 2410.

$C_{13}H_8O_3N_3Br_3$ ω-Bromonitrobenzaldehydedibromophenylhydrazones (CHATTAWAY and WALKER), 1695, 2411.

$C_{13}H_8O_3NBr_3$ *s*-Tribromophenyl *p*-nitrobenzyl ether (HOLMES and INGOLD), 1809.

$C_{13}H_8O_3N_3Cl_3$ β-Nitrobenzoyltrichlorophenylhydrazines (CHATTAWAY and WALKER), 1698.

$C_{13}H_8O_4NCl$ 3-Chloro-2-nitrophenyl benzoate (HODGSON and MOORE), 1601.

$C_{13}H_9O_2NCl_2$ Dichlorophenyl*cyclo*iminotoluquinones (CHATTAWAY and PARKES), 1311.

$C_{13}H_9O_2NBr_2$ 2:4-Dibromophenyl*cyclo*iminotoluquinone (CHATTAWAY and PARKES), 1311.

$C_{13}H_9O_3N_3Cl_2$ ω-Chloronitrobenzaldehydechlorophenylhydrazones (CHATTAWAY and WALKER), 1690.

$C_{13}H_9O_3N_3Br_2$ ω-Bromonitrobenzaldehydebromophenylhydrazones (CHATTAWAY and WALKER), 1695.

$C_{13}H_9O_2N_4Cl_3$ Nitrobenzaldehydetrichlorophenylhydrazidines (CHATTAWAY and WALKER), 1694.

$C_{13}H_9O_3N_3Br_2$ 4:6-Dibromo-3-hydroxybenzaldehyde-*p*-nitrophenylhydrazone (HODGSON and BEARD), 881.

β-Nitrobenzoyldibromophenylhydrazines (CHATTAWAY and WALKER), 1698.

$C_{13}H_9N_2ClBr_2$ ω-Chlorobenzaldehyde-2:4-dibromophenylhydrazone (CHATTAWAY and WALKER), 981.

$C_{13}H_{10}O_2NCl$ *p*-Chlorophenyl*cyclo*iminotoluquinone (CHATTAWAY and PARKES), 1311.

$C_{13}H_{10}O_2NBr$ *p*-Bromophenyl*cyclo*iminotoluquinone (CHATTAWAY and PARKES), 1311.

$C_{13}H_{10}O_2N_4Cl_2$ *m*-Nitrobenzaldehyde-2:4-dichlorophenylhydrazidine, and its hydrochloride (CHATTAWAY and WALKER), 1694.

$C_{13}H_{10}O_2N_4Br_2$ Nitrobenzaldehydedibromophenylhydrazidines, and their hydrochlorides (CHATTAWAY and WALKER), 1697.

$C_{13}H_{10}O_2Cl_2S_2$ 4-Tolyl 2:5-dichlorobenzenethiolsulphonate (GIBSON, MILLER, and SMILES), 1824.

$C_{13}H_{10}O_3N_3Br$ Bromohydroxybenzaldehyde-*p*-nitrophenylhydrazones (HODGSON and BEARD), 881.

$C_{13}H_{10}O_5N_3As$ Dinitrobenzoyl-4-aminophenylarsinic acids (KING and MURCH), 2637.

$C_{13}H_{10}N_2Br_2S$ 1-Anilinobenzthiazole tribromide (HUNTER), 2025.

$C_{13}H_{11}O_2NS_2$ Benzyl 2-nitrophenyl disulphide (FOOTNER and SMILES), 2889.

$C_{13}H_{11}O_2N_4Cl$ *m*-Nitrobenzaldehyde-*p*-chlorophenylhydrazidine (CHATTAWAY and WALKER), 1694.

$C_{13}H_{11}O_2N_4Br$ Nitrobenzaldehydebromophenylhydrazidine, and their hydrochlorides (CHATTAWAY and WALKER), 1697.

$C_{13}H_{11}O_4NS_2$ 2-Nitrophenyl 4-toluenethiolsulphonate (MILLER and SMILES), 229.
4-Tolyl 3-nitrobenzenethiolsulphonate (GIBSON, MILLER, and SMILES), 1822.

$C_{13}H_{11}O_7N_2As$ 3′-Nitro-4′-hydroxybenzoyl-4-aminophenylarsinic acid (KING and MURCH), 2649.

$C_{13}H_{13}O_5N_2As$ 3′-Amino-4′-hydroxybenzoyl-4-aminophenylarsinic acid, and its sodium salt (KING and MURCH), 2650.

$C_{13}H_{13}O_6N_2As$ 3′-Nitro-4′-toluoyl-4-aminophenyl (KING and MURCH), 2639.

$C_{13}H_{14}O_2NBr$ 8-Bromo-5:6-dimethoxy-2:4-dimethylquinoline, and its hydrochloride (LIONS, PERKIN, and ROBINSON), 1165.

$C_{13}H_{14}O_2Cl_2Te$ 4-Benzyl-2-methyl*cyclo*telluripentane-3:5-dione 1:1-dichloride (MORGAN and CORBY), 2618.

$C_{13}H_{14}O_4N_2As$ 3:3′-Diaminobenzoyl-4-aminophenylarsinic acid (KING and MURCH), 2638.

$C_{13}H_{16}O_3NBr$ β-6-Bromo-3:4-dimethoxyanilinopropenyl methyl ketone (LIONS, PERKIN, and ROBINSON), 1164.

$C_{13}H_{17}O_2N_2Br$ Bromomalonmono*iso*propylmono-*p*-tolylamide (WEST), 752.

$C_{13}H_{18}ON_2S$ 2-*m*-Xylidino-5-ethoxy-4:5-dihydrothiazole, and its picrate (NIMKAR and PYMAN), 2746.

$C_{13}H_{20}O_2NBr$ Diethylammonium β-bromo-β-phenylpropionate (SENTER and WARD), 1849.

$C_{13}H_{20}O_2NI$ γ-Piperonylpropyltrimethylammonium iodide (BAKER and ROBINSON), 1429.

13 V

$C_{13}H_7O_2N_3Cl_3Br$ ω-Bromo-*o*-nitrobenzaldehydetrichlorophenylhydrazones (CHATTAWAY and WALKER), 2412.

$C_{13}H_8O_2N_3Cl_2Br$ ω-Bromo-*o*-nitrobenzaldehyde-2:4-dichlorophenylhydrazone (CHATTAWAY and WALKER), 2411.

$C_{13}H_9O_2N_3ClBr$ ω-Bromo-*m*-nitrobenzaldehyde-*p*-chlorophenylhydrazone (CHATTAWAY and WALKER), 1695.

$C_{13}H_9O_8N_2ClAs$ 4′-Chloro-3:3′-dinitrobenzoyl-4-aminophenylarsinic acid (KING and MURCH), 2647.

$C_{13}H_{10}O_6N_2ClAs$ 4′-Chloro-3′-nitrobenzoyl-4-aminophenylarsinic acid (KING and MURCH), 2647.

$C_{13}H_{12}O_4N_2ClAs$ 4′-Chloro-3′-aminobenzoyl-4-aminophenylarsinic acid, and its salts (KING and MURCH), 2647.

$C_{13}H_{13}O_4N_3ClAs$ 4′-Chloro-3:3′-diaminobenzoyl-4-aminophenylarsinic acid (KING and MURCH), 2648.

C_{14} Group.

$C_{14}H_5Cl_9$ Nonochlorophenyltolylmethane (SILBERRAD), 2684.
$C_{14}H_8O_2$ Phenanthraquinone, action of hydrazine hydrate on (DUTT), 2971.
$C_{14}H_{10}O_4$ 2:4-Dihydroxybenzil (MARSH and STEPHEN), 1636.
$C_{14}H_{10}O_5$ 2:4:6-Trihydroxybenzil (MARSH and STEPHEN), 1637.
$C_{14}H_{12}O_6$ Acid, from ethyl dibromocinnamate and ethyl sodiomalonate (HAERDI and THORPE), 1247.
$C_{14}H_{14}O_2$ Methylbenzoin (ROGER), 523.
$C_{14}H_{15}As$ Phenyl-*p*-tolylmethylarsine (HUNT and TURNER), 2668.
$C_{14}H_{16}O_8$ Carbethoxyvanillylsuccinic acid (BAKER and LAPWORTH), 565.
$C_{14}H_{18}O_4$ β-Phenyl-β-methylpropane $\alpha\gamma$-diacetate (MILLS and BAINS), 2504.
$C_{14}H_{20}O_5$ Ethyl 1-methyl*cyclo*hexan-3-one-4-carboxylate-1-acetate (FARMER and ROSS), 2366.
$C_{14}H_{22}O_5$ Ethyl 1-methyl*cyclo*hexan-3-one-4-carboxylate-1-acetate (FARMER and ROSS), 2364.
$C_{14}H_{22}O_9$ $\delta\epsilon$-Dicarbethoxy-δ-hydroxy-$\gamma\gamma$-dimethylpentane-β-carboxylactone (ROTHSTEIN, STEVENSON, and THORPE), 1078.
$C_{14}H_{26}O_2$ *n*-Undecoylacetone, and its copper salt (MORGAN and HOLMES), 2893.
$C_{14}H_{26}O_3$ *l*-Menthyl ethoxyacetate (RULE and SMITH), 2191.

14 III

$C_{14}H_8O_9N_4$ Picryl-3:4-methylenedioxybenz*syn*aldoxime (BRADY and KLEIN), 846.
$C_{14}H_9N_2Br_2$ ω-Cyanobenzaldehyde-2:4-dibromophenylhydrazone (CHATTAWAY and WALKER), 982.
$C_{14}H_{10}O_4N$ Benzoyl-3:4-methylenedioxy-α-benzaldoxime (BRADY and MCHUGH), 2420.
$C_{14}H_{10}O_4N_2$ Benzoylnitro-α-benzaldoximes (BRADY and MCHUGH), 2420.
$C_{14}H_{10}O_5N_2$ 2:4-Dinitro-2′-hydroxystilbene (GULLAND and ROBINSON), 1503.
$C_{14}H_{10}O_6N_2$ 3:5-Dinitro-*o*-tolyl benzoate (GIBSON), 47.
$C_{14}H_{10}O_8N_4$ Picrylmethoxybens*syn*aldoximes (BRADY and KLEIN), 846.
$C_{14}H_{11}O_3N$ Phenyl-4-pyridylpyruvic acid (SINGH), 2448.
$C_{14}H_{11}O_4N$ Nitro-*o*-tolyl benzoates (GIBSON), 46.
$C_{14}H_{11}O_4N_3$ Nitrobenzylidenenitrobenzylamines (INGOLD), 1143.
$C_{14}H_{12}O_3N_4$ Phthalaldehyde 1-oxime-2-*p*-nitrophenylhydrazone (GRIFFITHS and INGOLD), 1705.
$C_{14}H_{12}O_5N_4$ 4-Nitro-3-methoxybenzaldehyde-*p*-nitrophenylhydrazone (HODGSON and BEARD), 881.
$C_{14}H_{12}N_2Cl_2$ Acetophenone-2:4-dichlorophenylhydrazone (HUMPHRIES, HUMBLE, and EVANS), 1306.
$C_{14}H_{12}N_2S$ 4′-Amino-1-methyl-5-methylbenzthiazole, bromination of (HUNTER), 1318.
$C_{14}H_{13}ON_3$ Benzeneazobenzylformaldoxime (WALKER), 1860.
$C_{14}H_{13}OAs$ 10-Ethylphenoxarsine (AESCHLIMANN), 813.
$C_{14}H_{13}O_2N$ *o*-Acetylaminodiphenyl ether (ROBERTS and TURNER), 2008.
o-Tolyl*cyclo*iminotoluquinone (CHATTAWAY and PARKES), 1310.
$C_{14}H_{13}O_2N_3$ Tolualdehyde *p*-nitrophenylhydrazones (STEPHEN), 1877.
$C_{14}H_{13}O_2As$ *o*-Carboxydiphenylmethylarsine (AESCHLIMANN), 812.
10-Ethylphenoxarsine oxide ($+H_2O$) (AESCHLIMANN), 814.
$C_{14}H_{13}O_3As$ *o*-Carboxydiphenylmethylarsine oxide (AESCHLIMANN), 813.
$C_{14}H_{13}O_4N_3$ Dinitrodibenzylamines, and their salts (HOLMES and INGOLD), 1815.
$C_{14}H_{14}ON_2$ 2-Hydroxy-3:3′-dimethylazobenzene (CUMMING and FERRIER), 2377.
$C_{14}H_{14}O_4S_5$ Phenylmethylsulphone *m*-disulphide (TWIST and SMILES), 1251.

$C_{14}H_{14}O_4Te_2$ Bis-2-hydroxy-1-methoxyphenyl 4:4-ditelluride (MORGAN and DREW), 2314.

$C_{14}H_{14}O_6S_4$ Phenylmethylsulphone *m*-disulphoxide (TWIST and SMILES), 1251.

$C_{14}H_{14}IAs$ Diphenylylenedimethylarsonium iodide (AESCHLIMANN, LEES, MCCLELAND, and NICKLIN), 69.

$C_{14}H_{15}ON_3$ Lutidineazoanisole, and its hydrochloride (GULLAND and ROBINSON), 1496.

$C_{14}H_{15}O_3N$ γ-4-Hydroxy-2-methylquinoline-3-butyric acid (PATERSON and PLANT), 1798.

$C_{14}H_{15}O_6N_3$ Acetodinitrodibenzylamides (HOLMES and INGOLD), 1820.

$C_{14}H_{16}O_6S$ Thioindican (CRAIK and MACBETH), 1639.

$C_{14}H_{17}O_2N$ Substance, from dehydroeseretholemethine methiodide and silver oxide (STEDMAN and BARGER), 255.

$C_{14}H_{17}O_4N$ δ-*o*-Acetylaminobenzoylvaleric acid (PATERSON and PLANT), 1798.

$C_{14}H_{17}O_4N_3$ β-Methylpimelic-β-acetic acid (FARMER and ROSS), 2368.

$C_{14}H_{19}ON$ Ethylpentenoic acid *p*-toluidide (KON and LINSTEAD), 622.

$C_{14}H_{19}O_2N$ Etheserolene, picrate of (STEDMAN and BARGER), 257.

5-Ethoxy-1:3-dimethyl-3-ethyl-2-indoline (STEDMAN and BARGER), 251, 255.

$C_{14}H_{19}O_6N$ Ethyl 2-cyano*cyclo*butane-1:2:3-tricarboxylate (ING and PERKIN), 2396.

$C_{14}H_{19}O_{12}N$ Tetra-acetyl glucose 6-nitrate (OLDHAM), 2843.

$C_{14}H_{20}O_2N_2$ Malonmono*iso*butylmono-*p*-tolylamide (WEST), 751.

$C_{14}H_{21}O_3N_3$ *n*-Octaldehyde *p*-nitrophenylhydrazone (STEPHEN), 1875.

$C_{14}H_{23}O_2N$ β-Anilinobutaldehyde diethylacetal (MASON), 1033.

$C_{14}H_{27}ON_3$ Acetone-δ-menthylsemicarbazone (WILSON and CRAWFORD), 106.

14 IV

$C_{14}H_6O_3NBr_3$ 2:3:9-Tribromo-9-nitroanthrone (BARNETT), 2044.

$C_{14}H_8O_4N_2Cl_2$ Dichloro-9:10-dinitro-9:10-dihydroanthracenes (BARNETT), 2042.

$C_{14}H_8N_2Br_4S_2$ 1:1-Bisbenzthiazole tetrabromide (HUNTER), 1320.

$C_{14}H_9O_4N_2Cl_3$ 1:5:9-Trichloro-9:10-dinitro-9:10-dihydroanthracene (BARNETT), 2044.

$C_{14}H_9O_4N_2Br$ 9-Bromo-9:10-dinitro-9:10-dihydroanthracene (BARNETT), 2043.

$C_{14}H_9NIS$ 1-Phenylbenzthiazole methiodide (CLARK), 974.

$C_{14}H_{11}OCl_3Te$ Tellurium phenylbenzylketone trichloride (MORGAN and ELVINS), 2631.

$C_{14}H_{13}O_3Cl_3S_2$ 4-Chloroanisole 2-disulphide (GAUNTLETT and SMILES), 2746.

$C_{14}H_{12}O_3N_3Br$ Bromomethoxybenzaldehyde-*p*-nitrophenylhydrazones (HODGSON and BEARD), 881.

$C_{14}H_{12}O_4Cl_2S_2$ 4-Chloroanisole-2-disulphoxide (GAUNTLETT and SMILES), 2746.

$C_{14}H_{12}O_8N_2As$ 3:3′-Dinitro-4′-toluoyl-4-aminophenylarsinic acid (KING and MURCH), 2640.

$C_{14}H_{12}O_9N_2As$ Dinitro-4′-anisoyl-4-aminophenylarsinic acids (KING and MURCH), 2644.

$C_{14}H_{13}O_3N_2Cl$ Phenylpyridylpyruvic acid oxime hydrochloride (SINGH), 2448.

$C_{14}H_{13}O_5NS$ Nitro-*o*-tolyl toluene-*p*-sulphonates (GIBSON), 47.

$C_{14}H_{13}O_5SAs$ Sulpho-10-ethylphenoxarsine oxide (AESCHLIMANN), 814.

$C_{14}H_{13}O_7N_2As$ 3′-Nitro-4′-anisoyl-4-aminophenylarsinic acid (KING and MURCH), 2641.

$C_{14}H_{15}O_2NS$ *p*-Toluenesulphonbenzylamide (HOLMES and INGOLD), 1812.

$C_{14}H_{15}O_5N_2As$ 3′-Amino-4′-anisoyl-4-aminophenylarsinic acid, and its salts (KING and MURCH), 2642.

$C_{14}H_{15}BrIAs$ *p*-Bromodiphenyldimethylarsonium iodide (HUNT and TURNER), 2670.

$C_{14}H_{16}O_4N_3As$ 3:3'-Diamino-4'-toluoyl-4-aminophenylarsinic acid (KING and MURCH), 2640.

$C_{14}H_{16}N_2Cl_6Sn$ Benzaldehyde stannichloride (STEPHEN), 1876.

$C_{14}H_{19}O_2N_2Br$ Bromomalonmono*iso*butylmono-*p*-tolylamide (WEST), 752.

$C_{14}H_{22}O_2N_2S$ α-Propionacetalylphenylthiocarbamide (BURTLES, PYMAN, and ROYLANCE), 589.

C_{15} Group.

$C_{15}H_{18}$ Tri*cyclo*trimethylenebenzene (PERKIN and PLANT), 1140.

$C_{15}H_{24}$ Hydrocarbon, from cedrene and formic acid (ROBERTSON, KERR, and HENDERSON), 1946.

Hydrocarbon, from formic acid and cadinene (ROBERTSON, KERR, and HENDERSON), 1946.

15 II

$C_{15}H_{10}O_4$ Alizarin 2-methyl ether (KUBOTA and PERKIN), 1893.

$C_{15}H_{10}O_5$ Anthragallol methyl ethers (KUBOTA and PERKIN), 1893.

$C_{15}H_{10}O_6$ Datiscetin, synthesis of (KALFF and ROBINSON), 1968.

$C_{15}H_{11}N$ α-Acenaphthaquinoline, and its picrate (STEWART), 1331.

$C_{15}H_{12}O_2$ Phenyl benzyl diketone (MALKIN and ROBINSON), 369.

$C_{15}H_{12}O_3$ Hydroxymethoxyanthrones (MILLER and PERKIN), 2688.

$C_{15}H_{12}O_5$ Dihydroxymethoxybenzils (MARSH and STEPHENS), 1636.

$C_{15}H_{12}O_6$ Trihydroxymethoxybenzils (MARSH and STEPHEN), 1637.

$C_{15}H_{13}N$ 1-Methyl-2-methylene-1:2-dihydro-β-naphthaquinoline (MILLS and RAPER), 2472.

$C_{15}H_{14}O_3$ α-Benzylmandelic acid (MALKIN and ROBINSON), 374.

$C_{15}H_{14}O_4$ Benzylphloracetophenone (BAKER), 2355.

$C_{15}H_{14}O_5$ Dihydroxyphenyl β-dihydroxyphenylethyl ketones (CHAPMAN and STEPHEN), 891.

Ethyl α-acetyl-γ-hydroxy-γ-phenyl-Δ^{β}-propenecarboxylactone (R. M. and J. N. RÂY), 2722.

$C_{15}H_{16}O_4$ Lactone, from ethyl sodioethylmalonate and phenacyl bromide (R. M. and J. N. RÂY), 2723.

$C_{15}H_{17}N$ Dibenzylmethylamine, and its hydrochloride (HOLMES and INGOLD), 1816.

$C_{15}H_{18}O_5$ Methyl 2-ethoxy-3-phenyl*cyclo*propane-1:2-dicarboxylate (HAERDI and THORPE), 1243.

$C_{15}H_{20}O_2$ 2-Hydroxystyryl *n*-hexyl ketone (MCGOOKIN and SINCLAIR), 2543.

$C_{15}H_{22}O_3$ Ngaione (MCDOWALL), 2202.

$C_{15}H_{22}O_7$ Ethyl 2-acetyl*cyclo*butane-1:2:3-tricarboxylate (ING and PERKIN), 2397.

$C_{15}H_{24}O_3$ Ngaiol (MCDOWALL), 2205.

$C_{15}H_{28}O_2$ Lauroylacetone, and its copper salt (MORGAN and HOLMES), 2894.

$C_{15}H_{28}O_8$ Diacetalmalonic acid, and its barium salt (PERKIN and PINK), 192.

$C_{15}H_{30}O_6$ Hexamethyl glycerol glucoside (GILCHRIST and PURVES), 2740.

15 III

$C_{15}H_9O_4N$ α-Naphthaquinoline-6:7-dicarboxylic acid (STEWART), 1331.

$C_{15}H_9NS$ 9-Anthryl thiocyanate (FOOTNER and SMILES), 2890.

$C_{15}H_{10}O_3N_2$ Anhydro-2-aldehydoterephthalic acid phenylhydrazone (PERKIN and STONE), 2294.

$C_{15}H_{10}O_4N_2$ 3-Nitrophthal-*p*-tolil (BRADY, QUICK, and WELLING), 2267.

$C_{15}H_{10}O_6N_2$ 2:4-Dinitro-3':4'-methylenedioxystilbene (GULLAND and ROBINSON), 1502.

$C_{15}H_{10}O_7N_4$ Picrylcinnam*syn*aldoxime (BRADY and KLEIN), 847.

$C_{15}H_{11}O_3Cl$ Chrysinidin chloride ($+2H_2O$) (PRATT and ROBINSON), 1132.
$C_{15}H_{11}O_4Cl$ Apigeninidin chloride ($+2H_2O$) (PRATT and ROBINSON), 1133.
Galanginidin chloride (PRATT and ROBINSON), 1135; (MALKIN and ROBINSON), 1193.
$C_{15}H_{11}O_4I$ Galanginidin iodide (PRATT and ROBINSON), 1135.
$C_{15}H_{11}O_5Cl$ Datiscetinidin chloride ($+H_2O$) (PRATT and ROBINSON), 1185.
Fisetinidin chloride ($+\frac{1}{2}H_2O$) (PRATT and ROBINSON), 1136.
Lotoflavinidin chloride ($+2H_2O$) (PRATT and ROBINSON), 1134.
Luteolinidin chloride ($+2H_2O$) (PRATT and ROBINSON), 1135.
Pelargonidin chloride ($+H_2O$) (MALKIN and ROBINSON), 1194.
3:5:7:3′-Tetrahydroxyflavylium chloride (PRATT and ROBINSON), 1186.
$C_{15}H_{11}O_5N_3$ 4-Aldehydo-1:2-hydroxyphthalide *p*-nitrophenylhydrazone (PERKIN and STONE), 2293.
$C_{15}H_{11}O_6Cl$ Cyanidin chloride ($+H_2O$) (PRATT and ROBINSON), 172.
Morinidin chloride ($+2H_2O$) (PRATT and ROBINSON), 1137.
$C_{15}H_{11}O_7Cl$ Delphinidin chloride (PRATT and ROBINSON), 174, 1190.
$C_{15}H_{12}O_2N_2$ 4-Aldehydo-1:2-phthalide phenylhydrazone (PERKIN and STONE), 2290.
$C_{15}H_{12}O_4N_2$ 4-Aldehydophthalic acid phenylhydrazone (PERKIN and STONE), 2295.
Carbanilino-3:4-methylenedioxybenzaldoximes (BRADY and MCHUGH), 2424.
4-Nitro-2-amino-3′:4′-methylenedioxystilbene (GULLAND and ROBINSON), 1502.
$C_{15}H_{12}O_5N_2$ Phthal-2-nitro-*p*-toluidic acid (BRADY, QUICK, and WELLING), 2267.
$C_{15}H_{12}O_6N_2$ 2:4-Dinitro-3′-methoxy-4′-hydroxystilbene (GULLAND and ROBINSON), 1503.
$C_{15}H_{12}O_{10}N_2$ Trimethylene glycol bis-2:4-dinitrophenyl ether (FAIRBOURNE and FOSTER), 2762.
$C_{15}H_{13}O_2N$ Benzilmonoxime methyl ethers (BRADY and PERRY), 2876.
$C_{15}H_{13}O_3N$ Anisylidene-*p*-aminobenzoic acid (WAYNE and COHEN), 460.
Benzoyl-*o*-methoxy-*a*-benzaldoxime (BRADY and MCHUGH), 2421.
Phthalobenzylamic acid (HOLMES and INGOLD), 1810.
$C_{15}H_{13}O_7N_5$ Picryl-*p*-dimethylaminobenz*syn*aldoxime (BRADY and KLEIN), 847.
$C_{15}H_{14}O_3N_2$ Carbanilino-*o*-methoxy-*a*-benzaldoxime (BRADY and MCHUGH), 2425.
$C_{15}H_{14}N_2S$ 1-*m*-Toluidino-*m*-toluthiazole (HUNTER), 2027.
$C_{15}H_{15}ON_3$ Phenylpyruvic acid oxime (WALKER), 1862.
$C_{15}H_{15}O_2N_3$ Benzoinsemicarbazone (HOPPER), 1285.
p-Tolylacetaldehyde *p*-nitrophenylhydrazone (STEPHEN), 1877.
$C_{15}H_{15}O_4N_3$ Dinitrodibenzylmethylamines, and their hydrochlorides (HOLMES and INGOLD), 1817.
$C_{15}H_{17}ON$ *β*-Amino-*aa*-diphenyl-*n*-propyl alcohol (MCKENZIE and WILLS), 288.
$C_{15}H_{17}O_2N$ Benzylnorhydrohydrastinine, and its salts (HAWORTH, PERKIN, and PINK), 1721.
$C_{15}H_{18}O_4Br_2$ Ethyl *aa*′-dibromo-*β*-phenylglutarate (HAERDI and THORPE), 1241.
$C_{15}H_{18}IAs$ Phenyl-*p*-tolyldimethylarsonium iodide (HUNT and TURNER), 2668.
$C_{15}H_{19}O_7N_5$ Trinitroeserethole (STEDMAN and BARGER), 256.
$C_{15}H_{20}O_2N_2$ Substance, and its salts, from oxidation of eserethole (STEDMAN and BARGER), 256.
$C_{15}H_{20}O_5N_2$ 6-Nitro-1-acetyl-5:8-dimethoxy-2:4-dimethyl-1:2:3:4-tetrahydroquinoline (LIONS, PERKIN, and ROBINSON), 1163.
$C_{15}H_{21}O_2N_3$ Eserine (STEDMAN and BARGER), 247.
$C_{15}H_{21}O_3N$ Acetyl derivatives of dimethoxydimethyltetrahydroquinolines (LIONS, PERKIN, and ROBINSON), 1163.

$C_{15}H_{23}O_3N$ Ngaione oxime (McDowall), 2204.
$C_{15}H_{23}O_4N$ Veratrylideneaminoacetal (Forsyth, Kelly, and Pyman), 1665.
$C_{15}H_{25}O_4N$ Veratrylaminoacetal (Forsyth, Kelly, and Pyman), 1665.
$C_{15}H_{26}O_2Te$ 2-*n*-Decyl*cyclo*telluropentane-3:5-dione (Morgan and Taylor), 2620.

15 IV

$C_{15}H_7O_2NCl_4$ Tetrachlorophthal-*p*-tolil (Brady, Quick, and Welling), 2267.
$C_{15}H_9ONCl_6$ 2:4-Di(trichloromethyl)benzanilide (Perkin and Stone), 2296.
$C_{15}H_{10}O_3N_3Cl_3$ Acetyl-*m*-nitrobenzaldehydetrichlorophenylhydrazone (Chattaway and Walker), 1697.
$C_{15}H_{10}O_3N_3Br_3$ Acetyl-*m*-nitrobenzaldehydetribromophenylhydrazone (Chattaway and Walker), 1697.
$C_{15}H_{10}O_4N_3Cl_3$ α-Acetyl-β-nitrobenzoyltrichlorophenylhydrazines (Chattaway and Walker), 1693.
$C_{15}H_{10}O_4N_3Br_3$ α-Acetyl-β-nitrobenzoyltribromophenylhydrazine (Chattaway and Walker), 1696.
$C_{15}H_{11}ONCl_4$ 2:4-Di(dichloromethyl)benzanilide (Perkin and Stone), 2291.
$C_{15}H_{11}O_4N_3Cl_2$ α-Acetyl-β-nitrobenzoylchlorophenylhydrazines (Chattaway and Walker), 1693.
$C_{15}H_{11}O_4N_3Br_2$ α-Acetyl-β-nitrobenzoyldibromophenylhydrazines (Chattaway and Walker), 1696.
$C_{15}H_{12}O_4N_3Cl$ α-Acetyl-β-*p*-nitrobenzoyl-*p*-chlorophenylhydrazine (Chattaway and Walker), 1693.
$C_{15}H_{12}O_4N_3Br$ α-Acetyl-β-nitrobenzoylbromophenylhydrazines (Chattaway and Walker), 1696.
$C_{15}H_{12}N_2Br_2S$ Dibromo-1-toluidinomethylbenzthiazoles, and their salts (Hunter), 2026.
$C_{15}H_{14}N_2Br_4S$ 1-*p*-Toluidino-5-methylbenzthiazole tetrabromide (Hunter), 2027.
$C_{15}H_{14}N_2Br_6S$ 1-*o*-Toluidino-3-methylbenzthiazole hexabromide (Hunter), 2026.
$C_{15}H_{14}O_9N_3As$ Dinitro-4′-ethoxybenzoyl-4-aminophenylarsinic acids (King and Murch), 2646.
$C_{15}H_{15}O_6N_2As$ 3′-Acetylamino-4′-hydroxybenzoyl-4-aminophenylarsinic acid (King and Murch), 2651.
$C_{15}H_{15}O_7N_2As$ 3′-Nitro-4′-ethoxybenzoyl-4-aminophenylarsinic acid (King and Murch), 2646.
$C_{15}H_{15}N_2Br_7S$ 1-*m*-Toluidino-*m*-toluthiazole hexabromide hydrobromide (Hunter), 2027.
$C_{15}H_{16}OIAs$ 10-Methyl-10-ethylphenoxarsonium iodide (Aeschlimann), 814.
$C_{15}H_{17}O_2NS$ *p*-Toluenesulphonbenzylmethylamide (Holmes and Ingold), 1813.
$C_{15}H_{17}O_5N_2As$ 3′-Amino-4′-ethoxybenzoyl-4-aminophenylarsinic acid, and its salts (King and Murch), 2646.
$C_{15}H_{26}O_2Cl_2Te$ 2-*n*-Decyl*cyclo*telluripentane-3:5-dione 1:1-dichloride (Morgan and Taylor), 2620.

C_{16} Group.

$C_{16}H_{16}$ αγ-Diphenyl-γ-methyl-Δ$^{\alpha}$-propene (Trotman), 92.
$C_{16}H_{18}$ αγ-Diphenyl-β-methylpropane (Trotman), 93.

16 II

$C_{16}H_{10}N_2$ 1:6-Naphthadiquinoline (Armit and Robinson), 1614.
$C_{16}H_{12}O_3$ 7-Hydroxy-4-benzylcoumarin (Baker and Robinson), 1984.
7-Hydroxy-2-methyl*iso*flavone (Baker and Robinson), 1984.
7-Methoxy*iso*flavone (Baker and Robinson), 1986.

$C_{16}H_{12}O_4$ 5:7-Dihydroxy-2-methyl*iso*flavone (BAKER and ROBINSON), 1984.
7:8-Dihydroxy-3-phenyl-2-methylbenzo-γ-pyrone (BAKER), 2357.
$C_{16}H_{12}O_5$ Anthrapurpurin dimethyl ether (MILLER and PERKIN), 2690.
Galangin methyl ether (KALFF and ROBINSON), 182.
$C_{16}H_{12}O_7$ Quercetin methyl ether, and its potassium salt (KUBOTA and PERKIN), 1894.
$C_{16}H_{14}O_3$ 4-Methoxyphenyl benzyl diketone (MALKIN and ROBINSON), 375.
Phenyl 4-methoxybenzyl diketone (MALKIN and ROBINSON), 374.
$C_{16}H_{14}O_5$ Homopiperonylresacetophenone (BAKER and ROBINSON), 1430.
$C_{16}H_{16}O_3$ Benzylorcacetophenone (BAKER), 2356.
$C_{16}H_{16}O_4$ Methoxybenzylmandelic acids (MALKIN and ROBINSON), 376.
$C_{16}H_{17}N$ 1-Benzyl-1:2:3:4-tetrahydro*iso*quinoline, and its salts (FORSYTH, KELLY, and PYMAN), 1664.
$C_{16}H_{17}Br$ β-Bromo-α-phenyl-β-benzylpropane (TROTMAN), 92.
$C_{16}H_{18}O$ Dibenzylmethylcarbinol (TROTMAN), 92.
$C_{16}H_{18}O_2$ α-Hydroxy-β-methoxy-αγ-diphenylpropane (MALKIN and ROBINSON), 377.
$C_{16}H_{18}O_4$ Lactone, from ethyl sodio*iso*propylmalonate and phenacyl bromide (R. M. and J. N. RÂY), 2723.
$C_{16}H_{18}O_6$ Ethyl β-methylpimelate-β-acetate (FARMER and ROSS), 2363.
$C_{16}H_{19}As$ Phenylmesitylmethylarsine (HUNT and TURNER), 2669.
$C_{16}H_{20}N_2$ Diphenyl-βγ-diamino-*n*-butanes (MORGAN and SKINNER), 1734.
$C_{16}H_{24}O_8$ Ethyl *cyclo*butane-1:2:2:3-tetracarboxylate (ING and PERKIN), 2394.
$C_{16}H_{26}O_2$ Caryophyllene formate (ROBERTSON, KERR, and HENDERSON), 1945.
Ngaiol acetate (MCDOWALL), 2205.
$C_{16}H_{26}O_3$ Ngaiol methyl ether (MCDOWALL), 2206.
$C_{16}H_{30}O_2$ *n*-Tridecoylacetone, and its copper salt (MORGAN and HOLMES), 2894.
$C_{16}H_{30}O_3$ 4-Ketopalmitic acid (G. M. and R. ROBINSON), 180.
$C_{16}H_{32}O_2$ Palmitic acid, sodium salt, equilibria of, with water and sodium chloride (MCBAIN and LANGDON), 852.

16 III

$C_{16}H_{12}O_3N_2$ 6′-Aminopiperonylideneoxindole (ARMIT and ROBINSON), 1612.
$C_{16}H_{12}Cl_2As$ αα′-Dichlorodistyrylchloroarsine (HUNT and TURNER), 998.
$C_{16}H_{13}ON_2$ 2-Styryl-1-methyl-4-quinazolone (HEILBRON, KITCHEN, PARKES, and SUTTON), 2172.
$C_{16}H_{13}O_2N_3$ 2:3-Dimethoxyindophenazine, and its salts (ARMIT and ROBINSON), 1615.
$C_{16}H_{13}O_3Cl$ 5:7-Dihydroxy-2-phenyl-4-methylbenzopyrylium chloride, and its ferrichloride (WALKER and HEILBRON), 687.
$C_{16}H_{13}O_4Cl$ Galanginidin chloride 3-methyl ether ($+H_2O$) (MALKIN and ROBINSON), 1192.
$C_{16}H_{13}O_8N_3$ 2:4:6-Trinitro-3′:4′-dimethoxystilbene (GULLAND and ROBINSON), 1503.
$C_{16}H_{14}O_2Br_2$ Phenyl αβ-dibromo-α-methoxy-β-phenylethyl ketone (MALKIN and ROBINSON), 372.
$C_{16}H_{14}O_6N_2$ Dinitrodimethoxystilbenes (GULLAND and ROBINSON), 1502.
$C_{16}H_{14}O_7N_2$ Benzoyl derivative of trimethylene glycol monodinitrophenyl ether (FAIRBOURNE and FOSTER), 2762.
$C_{16}H_{15}O_3N$ Ethyl phenyl-4-pyridylpyruvate (SINGH), 2448.
$C_{16}H_{16}O_2N_2$ Benzildioxime dimethyl ethers (BRADY and PERRY), 2879.
Benzoyl-*p*-dimethylamino-α-benzaldoxime (BRADY and MCHUGH), 2421.
p-Dimethylaminobenzylidene-*p*-aminobenzoic acid (WAYNE and COHEN), 460.
Phenylpyruvic acid *p*-tolylhydrazone (WALKER), 1862.

$C_{16}H_{16}O_4N_2$ 2-Nitro-4-amino-2′:3′-dimethoxystilbene (GULLAND and ROBINSON), 1502.

$C_{16}H_{17}ON$ Acetodibenzylamide (HOLMES and INGOLD), 1819.

$C_{16}H_{17}O_2N$ *p*-Dimethylaminodiphenylacetic acid (SINGH), 2447.

$C_{16}H_{17}O_3N$ *p*-Dimethylaminobenzilic acid (SINGH), 2447.

$C_{16}H_{18}O_2Te_2$ Bis-*p*-phenetyl ditelluride (MORGAN and DREW), 2311.

$C_{16}H_{18}O_4Te_2$ Bis-1:3-dimethoxyphenyl 4:4-ditelluride (MORGAN and DREW), 2313.

$C_{16}H_{19}O_4N$ Divanillylamine, and its hydrochloride (JONES and PYMAN), 2596.

$C_{16}H_{20}O_4N_2$ Ethyl β-carbethoxy-γ-benzeneazo-Δβ-pentenoate (MACBETH and TRAILL), 1120.

$C_{16}H_{21}O_4N$ Ethyl *p*-dimethylaminobenzylidenemalonate (WAYNE and COHEN), 459.

$C_{16}H_{25}O_3N_3$ Ngaione semicarbazone (MCDOWALL), 2204.

$C_{16}H_{27}O_3N$ β-*p*-Ethoxyanilinobutaldehyde diethylacetal (MASON), 1034.

$C_{16}H_{32}N_2S$ γγ′-Dipiperidinodipropyl sulphide, and its picrate (BENNETT and HOCK), 2676.

16 IV

$C_{16}H_{10}OClAs$ 7-Chloro-αβ-naphthaphenoxarsine (AESCHLIMANN), 814.

$C_{16}H_{15}O_9N_2As$ 3′-Nitro-4′-ethylcarbonatobenzoyl-4-aminophenylarsinic acid (KING and MURCH), 2649.

$C_{16}H_{16}O_3BrAs$ 10-Carboxymethyl-10-ethylphenoxarsonium bromide (AESCHLIMANN), 814.

$C_{16}H_{17}O_2N_2Cl$ Anisylideneazine hydrochloride, and its reaction with stannic chloride (SHOESMITH and SLATER), 1490.

$C_{16}H_{17}O_4NS$ Toluene-*p*-sulphonylbenzylaminoacetic acid (CLEMO and PERKIN), 2307.

$C_{16}H_{17}O_6N_2As$ 3′-Acetylamino-4′-anisoyl-4-aminophenylarsinic acid (KING and MURCH), 2642.

$C_{16}H_{18}OIAs$ 10:10-Diethylphenoxarsonium iodide (AESCHLIMANN), 814.

$C_{16}H_{18}O_2Cl_2Te$ Bis-*p*-phenetyltelluridichloride (MORGAN and DREW), 2312.

$C_{16}H_{18}O_4Cl_2Te$ Bis-1:3-dimethoxyphenyl-4-telluridichloride (MORGAN and DREW), 2313.

$C_{16}H_{25}O_2N_3S$ Ngaione thiosemicarbazone, and its silver salt (MCDOWALL), 2203.

C_{17} Group.

$C_{17}H_{20}$ α-Phenyl-β-benzyl-β-methylpropane (TROTMAN), 94.

17 II

$C_{17}H_{10}O_3$ *iso*Benzalizarin (MILLER and PERKIN), 2690.

$C_{17}H_{12}O_4$ 3:7-Dihydroxy-2-styrylchromone (ROBINSON and SHINODA), 1975.

$C_{17}H_{12}O_5$ 3:5:7-Trihydroxy-2-styrylchromone (ROBINSON and SHINODA), 1977.

$C_{17}H_{14}O_3$ 7-Hydroxy-2-methyl*iso*flavone methyl ether (BAKER and ROBINSON), 1984.

$C_{17}H_{14}O_4$ Dihydroxy-3-benzyl-2-methylbenzo-γ-pyrones (BAKER), 2355.

3:7-Dihydroxy-2-β-phenylethylchromone (ROBINSON and SHINODA), 1977.

$C_{17}H_{14}O_6$ 3:4′-Dimethoxy-5:7-dihydroxyflavone (ROBINSON and SHINODA), 1980.

$C_{17}H_{16}O_3$ Benzylbenzoylacetone (TROTMAN), 94.

$C_{17}H_{16}O_3$ 4-Methoxyphenyl β-methoxystyryl ketone (MALKIN and ROBINSON), 375.

Phenyl β:4-dimethoxystyryl ketone (MALKIN and ROBINSON), 374.

$C_{17}H_{16}O_4$ Benzoylveratroylmethane, and its copper salt (GULLAND and ROBINSON), 1501.

4-Methoxyphenyl 4-methoxybenzyl diketone (MALKIN and ROBINSON), 375.

$C_{17}H_{16}O_5$ Homopiperonylpaeanol (BAKER and ROBINSON), 1430.
$C_{17}H_{16}O_7$ 2:4-Dihydroxy-3′:4′:5′-trimethoxybenzil (MARSH and STEPHEN), 1637.
$C_{17}H_{16}O_8$ 2:4:6-Trihydroxy-3′:4′:5′-trimethoxybenzil (MARSH and STEPHEN), 1637.
$C_{17}H_{18}O$ *as*-Dibenzylacetone (MILLS and AKERS), 2477.
$C_{17}H_{18}O_5$ 4:4′-Dimethoxy-α-benzylmandelic acid (MALKIN and ROBINSON), 377.
Homoveratrylresacetophenone (BAKER and ROBINSON), 1433.
$C_{17}H_{19}N$ 2-β-Phenylethyl-1:2:3:4-tetrahydro*iso*quinoline, and its hydrochloride (HAWORTH, PERKIN, and PINK), 1716.
$C_{17}H_{22}O_5$ Ethyl 2-ethoxy-3-phenyl*cyclo*propane-1:2-dicarboxylate (HAERDI and THORPE), 1243.
$C_{17}H_{22}N_2$ Di(β-phenylethylamino)methane (SHORT), 271.
$C_{17}H_{32}O_2$ Myristoylacetone, and its copper salt (MORGAN and HOLMES), 2894.
$C_{17}H_{32}O_3$ Ethyl 2-acetyl-*n*-tridecoate (G. M. and R. ROBINSON), 179.

17 III

$C_{17}H_{12}O_2N_2$ 10:11-Anhydro-7:8-methylenedioxyquinindoline 10-methohydroxide (ARMIT and ROBINSON), 1613.
$C_{17}H_{13}ON$ Oxy*iso*protoberberine (HAWORTH, PERKIN, and PINK), 1717.
$C_{17}H_{13}O_2N_3$ α-Naphthaldehyde *p*-nitrophenylhydrazone (STEPHEN), 1877.
$C_{17}H_{13}O_3N$ Coumarincarboxylic acid *p*-toluidide (WAYNE and COHEN), 457.
$C_{17}H_{13}O_6N_3$ Acetyl-4-aldehydo-1:2-hydroxyphthalide *p*-nitrophenylhydrazone (PERKIN and STONE), 2293.
$C_{17}H_{15}ON$ 3-Benzylidene-4-keto-6-methyl-1:2:3:4-tetrahydroquinoline (CLEMO and PERKIN), 2305.
$C_{17}H_{15}O_2N$ 2-β-Phenylethylhomophthalimide (HAWORTH, PERKIN, and PINK), 1715.
$C_{17}H_{18}O_2N_2$ Malonmonobenzylmono-*p*-tolylamide (WEST), 751.
$C_{17}H_{15}O_3N_3$ 2:3-Dimethoxy-5(or 11)-methyl*iso*indophenazine (ARMIT and ROBINSON), 1616.
$C_{17}H_{15}O_6Cl$ Datiscetinidin chloride 3:2′-dimethyl ether (PRATT and ROBINSON), 1185.
5:7-Dihydroxy-3:3′-dimethoxyflavylium chloride ($+H_2O$) (PRATT and ROBINSON), 1186.
Pelargonidin chloride 3:4′-dimethyl ether (MALKIN and ROBINSON), 1194.
Pelargonidin chloride 3:3′-dimethyl ether (PRATT and ROBINSON), 1187.
$C_{17}H_{17}ON$ 2-β-Phenylethyl-3:4-dihydro-1-*iso*quinolone (HAWORTH, PERKIN, and PINK), 1715.
$C_{17}H_{17}ON_3$ 2-Benzyl-1-hydrindone semicarbazone (MILLS and AKERS), 2478.
$C_{17}H_{17}O_3N$ *N*-β-Phenylethylhomophthalamic acid (HAWORTH, PERKIN, and PINK), 1716.
$C_{17}H_{17}O_3N_3$ Benzylidene-δ-3-carbethoxyphenylsemicarbazide (WILSON and CRAWFORD), 107.
2:3-Dimethoxy-5(or 11)-methyl*iso*indophenazine methohydroxide (ARMIT and ROBINSON), 1616.
$C_{17}H_{18}O_4N_2$ Nitro-3-methoxy-2-ethoxybenzylidene-*p*-toluidines (RUBENSTEIN), 2268.
$C_{17}H_{20}ON_2$ β-*o*-Toluidinopropiono-*o*-toluidide (CLEMO and PERKIN), 2303.
$C_{17}H_{21}O_5N$ Carboxycamphoranilic acids, and their molecular rotation (M. and R. SINGH), 1966.
$C_{17}H_{22}IAs$ Phenylmesityldimethylarsonium iodide (HUNT and TURNER), 2669.
$C_{17}H_{23}O_2N$ Benzoylmenthoneoximes (READ and COOK), 2786.
$C_{17}H_{24}O_4N_2$ 6-Acetylamino-1-acetyl-5:8-dimethoxy-2:4-dimethyl-1:2:3:4-tetrahydroquinoline (LIONS, PERKIN, and ROBINSON), 1163.
$C_{17}H_{26}O_2S_2$ Ngaiol methyl xanthate (McDOWALL), 2205.

17 IV

$C_{17}H_{14}ONBr$ 3-Benzylidene-4-keto-6-methyl-1:2:3:4-tetrahydroquinoline bromide (CLEMO and PERKIN), 2305.

$C_{17}H_{14}O_2Cl_5Fe$ 3-Chloro-8-ethoxy-2-phenylbenzopyrylium ferrichloride (RIDGWAY and ROBINSON), 767.

$C_{17}H_{15}O_4SAs$ Sulphophenyl-*α*-naphthylmethylarsine oxide (AESCHLIMANN), 813.

$C_{17}H_{17}O_2N_2Br$ Bromomalonmonobenzylmono-*p*-tolylamide (WEST), 751.

Bromomalon-*p*-toluidide (WEST), 752.

$C_{17}H_{17}O_3NS$ Toluene-*p*-sulphonyl-4-ketomethyl-1:2:3:4-quinolines (CLEMO and PERKIN), 2303.

$C_{17}H_{17}O_4NS$ Toluene-*p*-sulphonyl-6-methoxy-4-keto-1:2:3:4-tetrahydroquinoline (CLEMO and PERKIN), 2305.

$C_{17}H_{17}O_7N_2As$ 3′-Acetylamino-4′-acetoxybenzoyl-4-aminophenylarsinic acid (KING and MURCH), 2651.

$C_{17}H_{19}O_4NS$ Toluene-*p*-sulphonyl-*β*-toluidinopropionic acids (CLEMO and PERKIN), 2302.

$C_{17}H_{19}O_5NS$ Toluene-*p*-sulphonyl-*β*-*p*-anisidinopropionic acid (CLEMO and PERKIN), 2305.

$C_{17}H_{19}O_7N_2As$ 3′-Carbethoxyamino-4′-anisoyl-4-aminophenylarsinic acid (KING and MURCH), 2642.

$C_{17}H_{27}O_2N_2I$ Dehydroseretholemethine methiodide (STEDMAN and BARGER), 254.

17 V

$C_{17}H_{10}O_3NBrS$ Colouring matter, from isatin and 4-bromo-2-carboxy-5-methoxyphenylthiolacetic acid (GRIFFITH and HOPE), 995.

$C_{17}H_{16}O_3NClS$ Toluene-*p*-sulphonyl-3-chloro-4-ketomethyl-1:2:3:4-tetrahydroquinolines (CLEMO and PERKIN), 2304.

Toluene-*p*-sulphonyl-3-chloro-6-methoxydihydroquinoline (CLEMO and PERKIN), 2306.

C_{18} Group.

$C_{18}H_{12}O_3$ *n*- and *iso*-Benzalizarin methyl ethers (MILLER and PERKIN), 2689.

$C_{18}H_{12}O_7$ Diacetylanthragallol (KUBOTA and PERKIN), 1893.

$C_{18}H_{14}O_3$ *r*-Phenyl-*α*-naphthylglycollic acid, conversion of, into ketones, and its silver salt (MCKENZIE and TATTERSALL), 2522.

$C_{18}H_{14}O_4$ 7-Hydroxy-3-methoxy-2-styrylchromone (ROBINSON and SHINODA), 1975.

Acetyl derivative of 7-hydroxy-2-methyl*iso*flavone (BAKER and ROBINSON), 1984.

$C_{18}H_{14}O_5$ 7-Hydroxy-3-homopiperonyl-2-methylchromone (BAKER and ROBINSON), 1431.

3-Methoxy-5:7-dihydroxy-2-styrylchromone (ROBINSON and SHINODA), 1977.

$C_{18}H_{14}O_6$ 2:4-Diacetoxybenzil (MARSH and STEVEN), 1636.

$C_{18}H_{16}O_4$ 7-Hydroxy-3-methoxy-2-*β*-phenylethylchromone (ROBINSON and SHINODA), 1976.

$C_{18}H_{16}O_6$ 3:7:2′-Trimethoxy-5-hydroxyflavone (KALFF and ROBINSON), 1971.

$C_{18}H_{16}N_4$ 10:15-Diamino-1:8-dimethyldibenzocopyrine, and its hydrochloride (GULLAND and ROBINSON), 1500.

$C_{18}H_{18}O_3$ *β*-Phenylpropionic anhydride (ROBINSON and SHINODA), 1976.

$C_{18}H_{18}O_4$ 4-Methoxyphenyl *β*:4-dimethoxystyryl ketone (MALKIN and ROBINSON), 375.

$C_{18}H_{18}O_5$ 4:4′-Dicarboxy-3:3′-dimethyldibenzyl ether (PERKIN and STONE), 2286.

$C_{18}H_{20}O_5$ Camphoryl hydrogen phthalates (FORSTER and SHUKLA), 1859.

$C_{18}H_{32}O_{10}$ Di(trimethyl glucosan) (IRVINE and OLDHAM), 2919.

$C_{18}H_{34}O_2$ Oleic acid, synthesis of (G. M. and R. ROBINSON), 175; oxidation of (LAPWORTH and MOTTRAM), 1628, 1987.

n-Pentadecoylacetone, and its copper salt (MORGAN and HOLMES), 2894.

$C_{18}H_{34}O_3$ Lactarinic acid (G. M. and R. ROBINSON), 179.

$C_{18}H_{36}O_4$ Dihydroxystearic acid, oxidation of (LAPWORTH and MOTTRAM), 1987.

18 III

$C_{18}H_{11}O_5N$ 6:7:3′:4′-Bismethylenedioxy-9-ketoprotopapaverine, and its salts (BUCK, PERKIN, and STEVENS), 1470.

$C_{18}H_{12}OCl_2$ Phenyl-α-naphthylchloroacetyl chloride (MCKENZIE and TATTERSALL), 2526.

$C_{18}H_{12}O_5N_2$ Oxime of 6:7:3′:4′-bismethylenedioxy-9-ketoprotopapaverine (BUCK, PERKIN, and STEVENS), 1471.

$C_{18}H_{13}OCl$ Phenyl-α-naphthylacetyl chloride (MCKENZIE and TATTERSALL), 2527.

$C_{18}H_{13}O_3N$ 2:3-Methylenedioxyoxyprotoberberines (HAWORTH, PERKIN, and PINK), 1718.

$C_{18}H_{13}O_4N$ 6:7:3′:4′-Bismethylenedioxyprotopapaverine, synthesis of, and its picrate (BUCK, PERKIN, and STEVENS), 1462.

$C_{18}H_{13}O_5N$ 6:7:3′:4′-Bismethylenedioxy-9-hydroxyprotopapaverine (BUCK, PERKIN, and STEVENS), 1471.

6:7:3′:4′-Bismethylenedioxy-9-keto-3:4-dihydroprotopapaverine, and its salts (BUCK, PERKIN, and STEVENS), 1470.

$C_{18}H_{14}O_5N_2$ Oxime of 6:7:3′:4′-bismethylenedioxy-9-keto-3:4-dihydroprotopapaverine (BUCK, PERKIN, and STEVENS), 1470.

$C_{18}H_{15}O_2N$ 2:3-Methylenedioxydihydroprotoberberine, and its salts (HAWORTH, PERKIN, and PINK), 1722.

$C_{18}H_{15}O_3Cl$ 4′:7-Dihydroxy-2-styryl-4-methylbenzopyrylium chloride (HEILBRON, WALKER, and BUCK), 692.

$C_{18}H_{15}O_3N$ 2:3-Methylenedioxyoxydihydro*iso*protoberberine (HAWORTH, PERKIN, and PINK), 1719.

$C_{18}H_{15}O_4N$ 6:7:3′:4′-Bismethylenedioxy-3:4-dihydroprotopapaverine, and its picrate (BUCK, PERKIN, and STEVENS), 1466.

2-Homopiperonylhomophthalimide (HAWORTH, PERKIN, and PINK), 1717.

$C_{18}H_{15}O_4Cl$ 3′:4′:7-Trihydroxy-2-styryl-4-methylbenzopyrylium chloride (HEILBRON, WALKER, and BUCK), 693.

$C_{18}H_{15}O_5N$ Nitro-3′:4′-dimethoxy-2-benzylidene-1-hydrindone (LIONS, PERKIN, and ROBINSON), 1168.

$C_{18}H_{15}BrGe$ Triphenylgermanium bromide (MORGAN and DREW), 1763.

$C_{18}H_{16}O_2N_2$ 4′-Methoxy-2-styryl-3-methyl-4-quinazolone (HEILBRON, KITCHEN, PARKES, and SUTTON), 2171.

$C_{18}H_{16}O_3S_2$ 2:4-Xylyl 2-naphthalenethiolsulphonate (GIBSON, MILLER, and SMILES), 1824.

$C_{18}H_{16}O_3S_2$ 6-Methoxy-3-tolyl 2-naphthalenethiolsulphonate (GIBSON, MILLER, and SMILES), 1824.

$C_{18}H_{17}O_2N$ 2:3-Methylenedioxytetrahydroprotoberberines, and their salts (HAWORTH, PERKIN, and PINK), 1718.

$C_{18}H_{17}O_3Cl$ 5:7-Dimethoxy-2-phenyl-4-methylbenzopyrylium chloride, and its ferrichloride (WALKER and HEILBRON), 688.

$C_{18}H_{17}O_4N$ 6:7:3′:4′-Bismethylenedioxy-1:2:3:4-tetrahydroprotopapaverine, and its salts (BUCK, PERKIN, and STEVENS), 1467.

Piperonylidene-γ-piperonylpropylamine (BAKER and ROBINSON), 1429.

$C_{18}H_{17}O_5N$ *N*-Homopiperonylhomophthalamic acid (HAWORTH, PERKIN, and PINK), 1718.

$C_{18}H_{17}O_5Cl$ Fisetinidin chloride trimethyl ether (+ $2H_2O$) (PRATT and ROBINSON), 170.

$C_{18}H_{17}O_6Cl$ Cyanidin chloride 3:3′:4′-trimethyl ether (+1½H_2O) (PRATT and ROBINSON), 1189.

Morinidin chloride 3:2′:4′-trimethyl ether (PRATT and ROBINSON), 1188.

$C_{18}H_{18}O_2N_4$ Acetophenoneoxalyldihydrazone (WILSON and PICKERING), 966.

$C_{18}H_{18}O_4N_2$ *N*-Homopiperonylhomophthalamic acid amide (HAWORTH, PERKIN, and PINK), 1718.

$C_{18}H_{18}O_6N_6$ *αγ*-Dialdehydopropane-*β*-carboxylic acid di-*p*-nitrophenylhydrazone (PERKIN and PINK), 194.

$C_{18}H_{19}O_3N$ Benzylhydrohydrastinine, and its hydrochloride (HAWORTH, PERKIN, and PINK), 1721.

$C_{18}H_{19}O_3N$ Methyl *N*-*β*-phenylethylhomophthalamate (HAWORTH, PERKIN, and PINK), 1716.

$C_{18}H_{19}O_3N_3$ 2:3-Dimethoxy-6-methylindophenazine methohydroxide (ARMIT and ROBINSON), 1616.

$C_{18}H_{20}O_2N_2$ Ethyl phenylpyruvate *p*-tolylhydrazone (WALKER), 1862.

$C_{18}H_{20}O_4N_2$ 5-Nitro-2:3-diethoxybenzylidene-*p*-toluidine (RUBENSTEIN), 2269.

$C_{18}H_{21}O_3N$ Ethyl *p*-dimethylaminobenzilate (SINGH), 2446.

1-1′-Hydroxy*cyclo*pentane-1′-carboxylylanilino*cyclo*pentane-1-carboxylactone (PLANT and FACER), 2039.

$C_{18}H_{21}O_6Br$ Ethyl α-carbethoxy-α′-bromo-*β*-phenylglutaconate (HAERDI and THORPE), 1245.

$C_{18}H_{22}O_2S$ *γγ*′-Diphenoxydipropyl sulphide (BENNETT and HOCK), 2675.

$C_{18}H_{23}O_3N$ Ethyl 3-*p*-dimethylaminophenyl-5-methyl-Δ^5-*cyclo*hexen-1-one-2-carboxylate (HEILBRON, FORSTER, and WHITWORTH), 2165.

$C_{18}H_{25}O_4N$ Ethyl 3-*p*-dimethylaminophenyl-5-methyl*cyclo*hexan-5-ol-1-one-2-carboxylate (HEILBRON, FORSTER, and WHITWORTH), 2165.

$C_{18}H_{26}O_6$ Ethyl Δ^1-*cyclo*hexene-1-acetate-2-malonate (BAKER), 988.

$C_{18}H_{27}ON_3$ Benzylidene-δ-menthylsemicarbazide (WILSON and CRAWFORD), 106.

$C_{18}H_{27}O_3N$ 9-Carbethoxynonanilide (G. M. and R. ROBINSON), 177.

$C_{18}H_{37}ON$ Acetohexadecylamide (ADAM and DYER), 73.

18 IV

$C_{18}H_{10}O_4S_2Br_2$ 5:5′-Dibromo-6:6′-dimethoxy-2:2′-bisoxythionaphthen (GRIFFITH and HOPE), 990.

$C_{18}H_{14}O_2NI$ 2:3-Methylenedioxyprotoberberinium iodide (HAWORTH, PERKIN, and PINK), 1722.

$C_{18}H_{14}O_3NCl$ 3-Chloro-2-homopiperonyl-1-*iso*quinolone (HAWORTH, PERKIN, and PINK), 1717.

$C_{18}H_{16}O_3Cl_5Fe$ 3-Chloro-4′-methoxy-8-ethoxy-2-phenylbenzopyrylium ferrichloride (RIDGWAY and ROBINSON), 768.

$C_{18}H_{18}O_7N_2S$ 6′-Methylaminopiperonylideneoxindole methyl hydrogen sulphate (ARMIT and ROBINSON), 1612.

$C_{18}H_{19}O_4NS$ Toluene-*p*-sulphonyl-6-ethoxy-4-keto-1:2:3:4-tetrahydroquinoline (CLEMO and PERKIN), 2306.

$C_{18}H_{20}O_2N_2S_2$ 2:2′-Diacetylmethylaminodiphenyl disulphide (CLARK), 974.

$C_{18}H_{21}O_4NS$ Ethyl toluene-*p*-sulphonylbenzylaminoacetate (CLEMO and PERKIN), 2307.

$C_{18}H_{21}O_5NS$ Toluene-*p*-sulphonyl-*β*-*p*-phenetidinopropionic acid (CLEMO and PERKIN), 2306.

C_{19} Group.

$C_{19}H_{12}O_4$ Acetyl*iso*benzalizarin (MILLER and PERKIN), 2689.

$C_{19}H_{16}O$ Phenyl-α-naphthylacetone (MCKENZIE and TATTERSALL), 2528.

$C_{19}H_{16}O_5$ 1-Acetoxy-2-methoxyanthrone (MILLER and PERKIN), 2688.
7-Hydroxy-3-homopiperonyl-2-methylchromone methyl ether (BAKER and ROBINSON), 1432.
$C_{19}H_{16}O_6$ 3:4′-Dimethoxy-5:7-dihydroxy-2-styrylchromone (ROBINSON and SHINODA), 1978.
$C_{19}H_{16}O_7$ Diacetoxymethoxybenzils (MARSH and STEPHEN), 1636.
$C_{19}H_{18}O_5$ 7-Hydroxy-3-homoveratryl-2-methylchromone (BAKER and ROBINSON), 1433.
$C_{19}H_{18}O_8$ 3:3′:4′:5′-Tetramethylmyricetin (KALFF and ROBINSON), 183.
$C_{19}H_{18}N_2$ *p*-Dimethylaminobenzylidene-β-naphthylamine (WAYNE and COHEN), 460.
$C_{19}H_{20}O_2$ 3:3-Dibenzylacetylacetone (MORGAN and TAYLOR), 802.
$C_{19}H_{26}O_8$ Ethyl diacetalmalonate (PERKIN and PINK), 192.
$C_{19}H_{36}O_2$ Palmitoylacetone, and its copper salt (MORGAN and HOLMES), 2895.
$C_{19}H_{38}O_6$ Acid, and its derivatives, from saponification of cutin (LEGG and WHEELER), 1419.

19 III

$C_{19}H_{13}O_5N$ Bismethylenedioxyoxyprotoberberine (BUCK, PERKIN, and STEVENS), 1469.
$C_{19}H_{13}N_2Cl_3$ Benzophenone-2:4:6-trichlorophenylhydrazone (HUMPHRIES, HUMBLE, and EVANS), 1306.
$C_{19}H_{14}O_4N$ 2:3:10:11-Bismethylenedioxyprotoberberine, synthesis of, and its salts (BUCK, PERKIN, and STEVENS), 1468.
$C_{19}H_{14}N_2Cl_2$ Benzophenone-2:4-dichlorophenylhydrazone (HUMPHRIES, HUMBLE, and EVANS), 1306.
$C_{19}H_{14}N_4Br_2$ Dibromoformazylbenzene (CHATTAWAY and WALKER), 982.
$C_{19}H_{15}ON$ *N*-Phenylbenziminophenyl ether, molecular rearrangement of (CHAPMAN), 1992.
$C_{19}H_{15}ON_3$ 1-Keto-2-phenyl-3:5-dimethyl-1:2-dihydro-2:4:6-naphtha*iso*triazine (GULLAND and ROBINSON), 1498.
$C_{19}H_{15}O_2N$ *o*-Benzoylaminodiphenyl ether (TURNER and SHEPPARD), 546.
$C_{19}H_{15}O_4N$ Bismethylenedioxydihydroprotoberberine, and its picrate (BUCK, PERKIN, and STEVENS), 1469.
$C_{19}H_{16}O_3N_2$ 1-Cyano-6:7-dimethoxy-2-benzoyl-1:2-dihydro*iso*quinoline (HAWORTH and PERKIN), 1442.
$C_{19}H_{16}O_4N_2$ Methoxy-3′:4′-methylenedioxy-2-styryl-1-methyl-4-quinazolones (HEILBRON, KITCHEN, PARKES, and SUTTON), 2174.
$C_{19}H_{16}O_5Br_2$ 7-Hydroxy-3-homopiperonyl-2-methylchromone methyl ether dibromide (BAKER and ROBINSON), 1432.
$C_{19}H_{17}O_3Cl$ 7-Hydroxy-4′-methoxy-2-styryl-4-methylbenzopyrylium chloride (HEILBRON, WALKER, and BUCK), 693.
$C_{19}H_{17}O_4N$ 2:3:10:11-Bismethylenedioxytetrahydroprotoberberine (BUCK, PERKIN, and STEVENS), 1467.
$C_{19}H_{17}O_4Cl$ 4′:7-Dihydroxy-3′-methoxy-4-styryl-2-methylbenzopyrylium chloride (HEILBRON, WALKER, and BUCK), 693.
$C_{19}H_{18}O_2Te$ 4:4-Dibenzyl*cyclo*telluropentane-3:5-dione (MORGAN and TAYLOR), 803.
$C_{19}H_{18}O_3N_2$ 3′:4′-Dimethoxy-2-styryl-3-methyl-4-quinazolone (HEILBRON, KITCHEN, PARKES, and SUTTON), 2171.
$C_{19}H_{18}O_8N_6$ αγ-Dialdehydopropane-ββ-dicarboxylic acid di-*p*-nitrophenylhydrazone (PERKIN and PINK), 193.
$C_{19}H_{19}O_2N$ 2-β-Phenylethyl-4:4-dimethylhomophthalimide (HAWORTH, PERKIN, and PINK), 1715.

$C_{19}H_{19}O_5N$ Methyl *N*-homopiperonylhomophthalamate (HAWORTH, PERKIN, and PINK), 1718.

$C_{19}H_{19}O_7Cl$ Delphinidin chloride 3:3′:4′:5′-tetramethyl ether (PRATT and ROBINSON), 1189.

$C_{19}H_{20}O_6N_2$ 6′-Nitroveratrylnorhydrohydrastinine (HAWORTH and PERKIN), 1450.

$C_{19}H_{20}NI$ Benzylquinaldine ethiodide (MILLS and RAPER), 2474.

$C_{19}H_{21}O_4N$ Methyl β-toluidinobenzylmalonates (WAYNE and COHEN), 459.

$C_{19}H_{26}O_9N_4$ 4-Carbethoxybispiperidinium-1:1′-spiran picrate (MILLS and BAINS), 2506.

19 IV

$C_{19}H_{12}ON_2S_2$ Substance, from distyryl ketone and thiocyanogen (CHALLENGER and BOTT), 1041.

$C_{19}H_{14}ONCl$ *N*-Phenylbenziminochlorophenyl ethers (CHAPMAN), 1996.

$C_{19}H_{18}O_2Cl_2Te$ 4:4-Dibenzyl*cyclo*telluripentane-3:5-dione 1:1-dichloride (MORGAN and TAYLOR), 802.

$C_{19}H_{19}O_5NBr$ 6′-Bromohomoveratroylhomopiperonylamine (HAWORTH and PERKIN), 1451.

$C_{19}H_{19}O_5Cl_4Fe$ 5:7:2′:4′-Tetramethoxyflavylium ferrichloride (PRATT and ROBINSON), 1134.

$C_{19}H_{20}O_4NBr$ 6′-Bromoveratrylnorhydrohydrastinine, and its salts (HAWORTH and PERKIN), 1452.

$C_{19}H_{28}O_2NBr$ 4-Phenyl-4′-carbethoxybispiperidinium-1:1′-spiran bromides (MILLS and WARREN), 2512.

$C_{19}H_{28}O_2NI$ 4-Phenyl-4′-carbethoxybispiperidinium-1:1′-spiran iodides (MILLS and WARREN), 2512.

C_{20} Group.

$C_{20}H_{14}O_4$ Acetylbenzalizarin methyl ether (MILLER and PERKIN), 2689.

$C_{20}H_{14}O_8$ Triacetylanthragallol (KUBOTA and PERKIN), 1893.

$C_{20}H_{16}O_6$ 7-Acetoxy-3-homopiperonyl-2-methylchromone (BAKER and ROBINSON), 1431.

5:7-Diacetoxy-2-methyl*iso*flavone (BAKER and ROBINSON), 1985.

7:8-Diacetoxy-3-phenyl-2-methylbenzo-γ-pyrone (BAKER), 2357.

$C_{20}H_{16}O_7$ Diacetylgalangin 3-methyl ether (KALFF and ROBINSON), 182.

2-*o*-Methoxybenzylidene-4:6-diacetoxycoumaranone (KALFF and ROBINSON), 1969.

$C_{20}H_{16}O_8$ 2:4:6-Triacetoxybenzil (MARSH and STEPHEN), 1631.

$C_{20}H_{16}N_2$ Dimethyl-2:2′-diquinolyls, and their salts (CONOLLY), 2083.

$C_{20}H_{18}O_4$ 7-Acetoxy-3-benzyl-2:5-dimethylbenzo-γ-pyrone (BAKER), 2357.

7-Hydroxy-3-benzyl-2:5-dimethylbenzo-γ-pyrone (BAKER), 2357.

Lactone from ethyl sodiobenzylmalonate and phenacyl bromide (R. M. and J. N. RÂY), 2723.

$C_{20}H_{18}O_5$ 4-Methoxycinnamic anhydride (ROBINSON and SHINODA), 1977.

$C_{20}H_{18}O_6$ Diacetylanthrapurpurinanthranol dimethyl ether (MILLER and PERKIN), 2691.

3:7:4′-Trimethoxy-5-hydroxy-2-styrylchromone (ROBINSON and SHINODA), 1978.

$C_{20}H_{18}O_7$ 3:3′:4′-Trimethoxy-5:7-dihydroxy-2-styrylchromone (+H_2O) (ROBINSON and SHINODA), 1979.

$C_{20}H_{20}O_5$ 7-Methoxy-3-homoveratryl-2-methylchromone (BAKER and ROBINSON), 1433.

$C_{20}H_{20}O_6$ Ethyl benzoylveratroylacetate (GULLAND and ROBINSON), 1501.

$C_{20}H_{22}O_6$ Dibenzyl dimethoxysuccinate, rotation of (PATTERSON and FULTON), 2436.

$C_{20}H_{24}O_7$ Ethyl 2-benzoyl*cyclo*butane-1:2:3-tricarboxylate (Ing and Perkin), 2397.
$C_{20}H_{34}O_2$ Substance, from reduction of tagetone (Jones and Smith), 2539.
$C_{20}H_{38}O_2$ Margaroylacetone, and its copper salt (Morgan and Holmes), 2895.
$C_{20}H_{40}O_2$ Arachidic acid, synthesis of (Adam and Dyer), 70.
$C_{20}H_{43}N$ Eicosylamine, hydrochloride of (Adam and Dyer), 73.

20 III

$C_{20}H_{11}O_{15}N_7$ Picryl-3-methoxy-4-picryloxybenz*syn*aldoxime (Brady and Klein), 847.
$C_{20}H_{15}ON_3$ 2-α-4-Pyridylbenzyl-3-quinoxalone (Singh), 2449.
$C_{20}H_{15}N_2Cl$ 3-Chloro-2:2-diphenyl-1:2-dihydroquinoxaline (Ingold and Weaver), 385.
$C_{20}H_{16}O_2N_2$ α-Naphthacarbamylcinnamaldoximes (Brady and McHugh), 2426.
$C_{20}H_{16}O_7Br_2$ 2-*o*-Methoxybenzylidene-4:6-diacetoxycoumaranone dibromide (Kalff and Robinson), 1970.
$C_{20}H_{17}ON$ Substance, from *as*-diphenylethylene and nitrosobenzene, constitution of (Burkhardt, Lapworth, and Walkden), 2458.
$C_{20}H_{17}O_5N$ Oxyberberine, synthesis of (Perkin, Rây, and Robinson), 740.
$C_{20}H_{18}O_4N_2$ Iminoberberine, and its hydrochloride (Haworth, Perkin, and Pink), 1723.
$C_{20}H_{19}ON$ β-Amino-αα*β*-triphenylethyl alcohols (McKenzie and Wills), 290.
$C_{20}H_{19}O_3N_3$ 7-Methoxy-4′-dimethylamino-2-styryl-1-methyl-4-quinazolone (Heilbron, Kitchen, Parkes, and Sutton), 2175.
$C_{20}H_{19}O_4N$ Anhydro-7-demethylomethylpapaverinol (Haworth and Perkin), 1458.
2-Homopiperonyl-4:4-dimethylhomophthalimide (Haworth, Perkin, and Pink), 1717.
$C_{20}H_{19}O_6N$ 2-Homopiperonyl-6:7-dimethoxyhomophthalimide (Haworth, Perkin, and Pink), 1720.
$C_{20}H_{20}O_6N_2$ 6-Nitrotetrahydroberberine (Haworth and Perkin), 1451.
$C_{20}H_{21}O_4N$ 7-Demethylomethylpapaverine (Haworth and Perkin), 1458.
dl-Dicentrine, synthesis of, and its salts (Haworth, Perkin, and Rankin), 2022.
$C_{20}H_{21}O_5N$ 7-Demethylomethylpapaverinol (Haworth and Perkin), 1457.
6:7:2′:3′-Tetramethoxy-2-benzyl-1-*iso*quinolone (Haworth and Perkin), 1439.
6:7:3′:4′-Tetramethoxy-2-benzyl-1-*iso*quinolone (Haworth, Perkin, and Rankin), 1446.
$C_{20}H_{21}O_6Cl$ Cyanidin chloride pentamethyl ether, and its hydrochloride (Pratt and Robinson), 171.
$C_{20}H_{21}O_7N$ *N*-Homopiperonyl-4:5-dimethoxyhomophthalamic acid (Haworth, Perkin, and Pink), 1720.
$C_{20}H_{22}O_2N_2$ *trans*-1-Methyl*cyclo*propane-1:2-dicarboxylic acid di-*p*-toluidide (Ingold), 396.
$C_{20}H_{22}O_6N_2$ Ethyl β-*m*-nitroanilinobenzylmalonate (Wayne and Cohen), 456.
6:7-Methylenedioxy-2′:3′-dimethoxy-2-benzyl-1-nitromethyl-1:2:3:4-tetrahydro-*iso*quinoline (Haworth and Perkin), 1441.
6′-Nitroveratrylhydrohydrastinine, and its salts (Haworth, Perkin, and Rankin), 2021.
$C_{20}H_{23}O_4N$ 1-Veratrylhydrohydrastinine, and its salts (Haworth, Perkin, and Rankin), 2020.
$C_{20}H_{23}O_5N$ 1-Hydroxy-6:7:2′:3′-tetramethoxy-2-benzyl-1:2-dihydro*iso*quinoline (Haworth and Perkin), 1438.
1-Hydroxy-6:7:3′:4′-tetramethoxy-2-benzyl-1:2-dihydro*iso*quinoline (Haworth, Perkin, and Rankin), 1445.

$C_{20}H_{23}O_5N$ 6:7:2′:3′-Tetramethoxy-2-benzyl-3:4-dihydro-1-*iso*quinolone (HAWORTH and PERKIN), 1440.

$C_{20}H_{24}O_4N_2$ 6′-Aminoveratrylhydrohydrastinine, and its salts (HAWORTH, PERKIN, and RANKIN), 2021.

$C_{20}H_{24}O_5N_2$ Nitrosoamine of 7-demethylomethyltetrahydropapaverine (HAWORTH and PERKIN), 1459.

$C_{20}H_{25}O_4N$ 7-Demethylomethyltetrahydropapaverine, and its picrate (HAWORTH and PERKIN,) 1459.

6:7:2′:3′-Tetramethoxy-2-benzyl-1:2:3:4-tetrahydro*iso*quinoline (HAWORTH and PERKIN), 1439.

6:7:3′:4′-Tetramethoxy-2-benzyl-1:2:3:4-tetrahydro*iso*quinoline (HAWORTH, PERKIN, and RANKIN), 1446.

$C_{20}H_{25}O_5N$ 1-Hydroxy-6:7:2′:3′-tetramethoxy-2-benzyl-1:2:3:4-tetrahydro*iso*quinoline, and its salts (HAWORTH and PERKIN), 1440.

$C_{20}H_{26}O_2S$ $\gamma\gamma'$-Di-*p*-tolyloxydipropyl sulphide (BENNETT and HOCK), 2675.

$C_{20}H_{28}O_8N_4$ Ethyl 6-phenylhexahydro-1:2:3:4-tetrazine-1:2:3:4-tetracarboxylate (INGOLD and WEAVER), 386.

$C_{20}H_{33}O_2N_3$ Myristaldehyde *p*-nitrophenylhydrazone (STEPHEN), 1876.

$C_{20}H_{41}ON$ Aceto-octadecylamide (ADAM and DYER), 73.

20 IV

$C_{20}H_{18}O_5NCl$ 3-Chloro-2-homopiperonyl-6:7-dimethoxy-1-*iso*quinolone (HAWORTH, PERKIN, and PINK), 1720.

$C_{20}H_{20}O_3NCl$ 7-Hydroxy-4′-dimethylamino-2-styryl-4-methylbenzopyrylium chloride (HEILBRON, WALKER, and BUCK), 693.

$C_{20}H_{20}O_5NI$ 6:7-Methylenedioxy-3′:4′-dimethoxy-1-benzoyl-3:4-dihydro*iso*quinoline methiodide (HAWORTH, PERKIN, and RANKIN), 2020.

$C_{20}H_{21}O_6Cl_4Fe$ 3:5:7:2′:4′-Pentamethoxyflavylium ferrichloride (PRATT and ROBINSON), 1137.

$C_{20}H_{22}O_4NCl$ Ethyl β-*p*-chloroanilinobenzylmalonate (WAYNE and COHEN), 457.

$C_{20}H_{22}O_4NBr$ Ethyl β-*p*-bromoanilinobenzylmalonate (WAYNE and COHEN), 457.

6:7:2′:3′-Tetramethoxy-2-benzyl*iso*quinolinium bromide (HAWORTH and PERKIN), 1437.

6:7:3′:4′-Tetramethoxy-2-benzyl*iso*quinolinium bromide (HAWORTH, PERKIN, and RANKIN), 1445.

$C_{20}H_{22}O_4NI$ 6:7:2′:3′-Tetramethoxy-2-benzyl*iso*quinolinium iodide (HAWORTH and PERKIN), 1438.

6:7:3′:4′-Tetramethoxy-2-benzyl*iso*quinolinium iodide (HAWORTH, PERKIN, and RANKIN), 1445.

1-Veratryl-6:7-methylenedioxydihydro*iso*quinoline methiodide (HAWORTH, PERKIN, and RANKIN), 2020.

$C_{20}H_{24}O_2N_2S_2$ 2:2′-Diacetylethylaminodiphenyl disulphide (CLARK), 974.

$C_{20}H_{24}O_4NCl$ 6:7:3′:4′-Tetramethoxy-2-benzyl-3:4-dihydro*iso*quinolinium chloride (HAWORTH, PERKIN, and RANKIN), 1447.

$C_{20}H_{24}O_4NI$ 6:7:2′:3′-Tetramethoxy-2-benzyl-3:4-dihydro*iso*quinolinium iodide (HAWORTH and PERKIN), 1439.

6:7:3′:4′-Tetramethoxy-2-benzyl-3:4-dihydro*iso*quinolinium iodide (HAWORTH, PERKIN, and RANKIN), 1446.

$C_{20}H_{24}O_4NI_3$ 6:7:3′:4′-Tetramethoxy-2-benzyl-3:4-dihydro*iso*quinolinium periodide (HAWORTH, PERKIN, and RANKIN), 1447.

$C_{20}H_{24}O_4NS$ $\gamma\gamma'$-Dipropyl sulphide diphenylurethane (BENNETT and HOCK), 2673.

C_{21} Group.

$C_{21}H_{14}O_3$ 7-Hydroxy-2-phenyl*iso*flavone (BAKER and ROBINSON), 1985.
$C_{21}H_{14}O_4$ 7:8-Dihydroxy-2:3-diphenylbenzo-γ-pyrone (BAKER), 2357.
$C_{21}H_{14}O_5$ Diacetyl*iso*benzalizarin (MILLER and PERKIN), 2690.
$C_{21}H_{14}N_2$ 2-Phenylphenanthriminazole (SIRCAR and RAY), 1048.
$C_{21}H_{16}N_2$ 2-Phenyl-3-benzylquinoxaline (MALKIN and ROBINSON), 373.
$C_{21}H_{16}S_2$ Benzyl 9-anthryl disulphide (FOOTNER and SMILES), 2889.
$C_{21}H_{18}O_6$ Diacetoxy-3-benzyl-2-methylbenzo-γ-pyrones (BAKER), 2356.
$C_{21}H_{18}O_8$ Diacetoxydimethoxyflavone (KALFF and ROBINSON), 1971.
$C_{21}H_{18}O_9$ Triacetoxymethoxybenzils (MARSH and STEPHEN), 1637.
$C_{21}H_{20}O_2$ ααβ-Triphenylpropylene αβ-glycol (ROGER), 522.
$C_{21}H_{20}O_6$ 7-Acetoxy-3-homoveratryl-2-methylchromone (BAKER and ROBINSON), 1433.
$C_{21}H_{20}O_7$ 3:7:3′:4′-Tetramethoxy-5-hydroxy-2-styrylchromone (ROBINSON and SHINODA), 1979.
$C_{21}H_{20}O_9$ 2:4-Diacetoxytrimethoxybenzil (MARSH and STEPHEN), 1637.
$C_{21}H_{24}O_6$ ββ′-Dibenzyloxydiethylmalonic acid, and its salts (BENNETT), 1280.
$C_{21}H_{40}O_2$ Stearoylacetone, and its copper salt (MORGAN and HOLMES), 2895.

21 III

$C_{21}H_{12}O_3N_2$ Nitro-2-phenylphenanthroxazoles (SIRCAR and RAY), 1049.
$C_{21}H_{13}O_2N$ 2′-Hydroxy-2-phenylphenanthroxazole (SIRCAR and RAY), 1049.
$C_{21}H_{14}O_2N_2$ 1:4-*endo*-Keto-2-keto-3:3-diphenyltetrahydroquinoxaline (INGOLD and WEAVER), 384.
$C_{21}H_{14}O_5N_6$ Dinitro-derivative of anhydro-2:4-dialdehydobenzoic acid diphenylhydrazone (PERKIN and STONE), 2293.
$C_{21}H_{14}N_2S$ Naphthylaminonaphthathiazoles (HUNTER), 2272.
$C_{21}H_{16}ON_4$ Anhydro-2:4-dialdehydobenzoic acid diphenylhydrazone (PERKIN and STONE), 2292.
$C_{21}H_{16}O_2N_2$ Dianilinodialdehydobenzoic acid (PERKIN and STONE), 2292.
$C_{21}H_{18}O_2N_4$ Phenylcarbamate of benzeneazobenzylformaldoxime (WALKER), 1861.
$C_{21}H_{19}ON$ Benzoyldi-*p*-tolylamine (CHAPMAN), 1998.
N-*p*-Tolylbenzimino-*p*-tolyl ether (CHAPMAN), 1998.
$C_{21}H_{19}O_2N_3$ Benzoin-δ-phenylsemicarbazone (HOPPER), 1287.
$C_{21}H_{19}O_4N$ Ethyl diphenacylcyanoacetate (R. M. and J. N. RÂY), 2722.
$C_{21}H_{20}O_4N_2$ 2:4-Dihydroxyphenyl β-2:4-dihydroxyphenylethyl ketone phenylhydrazone (CHAPMAN and STEPHEN), 892.
$C_{21}H_{20}O_5N_2$ 1-Cyano-6:7:2′:3′-tetramethoxy-2-benzoyl-1:2-dihydro*iso*quinoline (HAWORTH and PERKIN), 1442.
$C_{21}H_{26}O_9S_3$ Glyceryl tribenzenesulphonate (FAIRBOURNE and FOSTER), 2762.
$C_{21}H_{21}ON$ *d*-β-Amino-αα-diphenyl-β-benzylethyl alcohol (MCKENZIE and WILLS), 293.
β-Amino-ααβ-triphenyl-β-methylethyl alcohol (MCKENZIE and WILLS), 292.
$C_{21}H_{22}O_2N_2$ Strychnine, aluminioxalate of (CHILD, ROBERTS, and TURNER), 2971.
$C_{21}H_{23}O_4N_2$ 1-Cyano-6:7:2′:3′-tetramethoxy-2-benzyl-1:2-dihydro*iso*quinoline (HAWORTH and PERKIN), 1438.
1-Cyano-6:7:3′:4′-tetramethoxy-2-benzyl-1:2-dihydro*iso*quinoline (HAWORTH, PERKIN, and RANKIN), 1446.
$C_{21}H_{23}O_5N$ Keto-7-demethylo-ψ-corydaline (HAWORTH and PERKIN), 1461.
$C_{21}H_{23}O_6N$ Ethyl β-carboxyanilinobenzylmalonates (WAYNE and COHEN), 456.
$C_{21}H_{23}O_7N$ Methyl *N*-homopiperonyl-4:5-dimethoxyhomophthalamate (HAWORTH, PERKIN, and PINK), 1720.

$C_{21}H_{23}O_7Cl$ Delphinidin chloride hexamethyl ether, ($+\frac{1}{2}H_2O$) and its salts (PRATT and ROBINSON), 174.

$C_{21}H_{24}O_4N_2$ 1-Cyano-6:7:2′:3′-tetramethoxy-2-benzyl-1:2:3:4-tetrahydro*iso*quinoline (HAWORTH and PERKIN), 1441.

1-Cyano-6:7:3′:4′-tetramethoxy-2-benzyl-1:2:3:4-tetrahydro*iso*quinoline (HAWORTH, PERKIN, and RANKIN), 1447.

$C_{21}H_{25}O_4N$ 7-Demethylo-ψ-corydaline (HAWORTH and PERKIN), 1460.

Ethyl β-anilino-*p*-tolylmalonate (WAYNE and COHEN), 455.

Ethyl β-toluidinobenzylmalonates (WAYNE and COHEN), 455.

$C_{21}H_{25}O_5N$ Ethyl β-anilinoanisylmalonate (WAYNE and COHEN), 458.

Ethyl β-anisidinobenzylmalonates (WAYNE and COHEN), 458.

$C_{21}H_{26}O_4N_2$ Demethylechitamine, and its hydrochloride (GOODSON and HENRY), 1646.

$C_{21}H_{26}O_5N_2$ 6:7:2′:3′-Tetramethoxy-2-benzyl-1:2:3:4-tetrahydro*iso*quinoline-1-carboxylamide (HAWORTH and PERKIN), 1443.

$C_{21}H_{26}O_6N_2$ 6:7:2′:3′-Tetramethoxy-2-benzyl-1-nitromethyl-1:2:3:4-tetrahydro*iso*quinoline (HAWORTH and PERKIN), 1440.

6:7:3′:4′-Tetramethoxy-2-benzyl-1-nitromethyl-1:2:3:4-tetrahydro*iso*quinoline (HAWORTH, PERKIN, and RANKIN), 1447.

$C_{21}H_{27}O_4N$ 6:7:2′:3′-Tetramethoxy-2-benzyl-1-methyl-1:2:3:4-tetrahydro*iso*quinoline, and its picrate (HAWORTH and PERKIN), 1442.

$C_{21}H_{27}O_4N_3$ Ngaione *p*-nitrophenylhydrazone (MCDOWALL), 2203.

$C_{21}H_{31}O_4N$ *O*-Aceto-*N*-undecenovanillylamide (JONES and PYMAN), 2598.

$C_{21}H_{44}ON_2$ Eicosylcarbamide (ADAM and DYER), 73.

21 IV

$C_{21}H_{12}N_2Br_2S$ Dibromo-2-α-naphthylamino-β-naphthathiazole (HUNTER), 2272.

$C_{21}H_{14}ON_2Cl_2$ 2:2-Dichloro-1:4-*endo*-keto-3:3-diphenyltetrahydroquinoxaline (INGOLD and WEAVER), 385.

$C_{21}H_{14}N_2Br_4S$ 2-α-Naphthylamino-8-naphthathiazole tetrabromide (HUNTER), 2272.

$C_{21}H_{14}N_2Br_6S$ Naphthylaminonaphthathiazole hexabromides (HUNTER), 2273.

$C_{21}H_{15}N_2Br_3S$ Naphthylaminonaphthatriazole tribromides (HUNTER), 2272.

$C_{21}H_{15}N_2Br_7S$ 2-α-Naphthylamino-β-naphthathiazole heptabromide (HUNTER), 2272.

$C_{21}H_{18}O_8N_3As$ 3″-Nitrobenzoyl-3′-amino-4′-anisoyl-4-aminophenylarsinic acid (KING and MURCH), 2644.

$C_{21}H_{20}O_6N_3As$ 3″-Aminobenzoyl-3′-amino-4′-anisoyl-4-aminophenylarsinic acid, and its salts (KING and MURCH), 2644.

$C_{21}H_{24}O_4NCl$ Dihydro-7-demethylo-ψ-dehydrocorydalinium chloride (HAWORTH and PERKIN), 1460.

$C_{21}H_{24}O_4NI$ Dihydro-7-demethylo-ψ-dehydrocorydalinium iodide (HAWORTH and PERKIN), 1460.

$C_{21}H_{27}O_{10}N_3S_2$ Dimethoxymethyl*iso*indophenazine dimethosulphate (ARMIT and ROBINSON), 1616.

C_{22} Group.

$C_{22}H_{16}O_3$ 7-Hydroxy-3-benzyl-2-phenylbenzo-γ-pyrone (BAKER), 2355.

$C_{22}H_{16}O_4$ Dihydroxy-3-benzyl-2-phenylbenzo-γ-pyrones (BAKER), 2356.

$C_{22}H_{22}O_7$ 3:4-Dimethoxycinnamic anhydride (ROBINSON and SHINODA), 1979.

$C_{22}H_{42}O_2$ *n*-Nonadecoylacetone, and its copper salt (MORGAN and HOLMES), 2896.

$C_{22}H_{44}O_2$ Behenic acid, sodium salt, state of, in solution (LAING), 2751.

22 III

$C_{22}H_{16}O_2N_2$ *o*-Phenoxybenzeneazo-β-naphthol (TURNER and SHEPPARD), 546.

$C_{22}H_{18}ON_2$ 2-*p*-Methoxyphenyl-3-benzylquinoxaline (MALKIN and ROBINSON), 375.

2-Phenyl-3-*p*-methoxybenzylquinoxaline (MALKIN and ROBINSON), 374.

$C_{22}H_{19}O_2N_3$ Benzilmono-δ-benzylsemicarbazone (HOPPER), 1286.

$C_{22}H_{20}O_2N_4$ Phenylpyruvic acid oxime phenylcarbamate (WALKER), 1862.

$C_{22}H_{21}O_2N_3$ Benzoin-δ-benzylsemicarbazone (HOPPER), 1287.

$C_{22}H_{23}O_9N_2$ Anhydrocotarnine-6-nitro-4:5-dimethoxyphthalide (RÂY and ROBINSON), 1621.

$C_{22}H_{23}O_3N$ 3-*p*-Dimethylamino-5-*o*-hydroxystyryl-Δ^5-*cyclo*hexen-1-one (HEILBRON, FORSTER, and WHITWORTH), 2164.

$C_{22}H_{23}O_6N$ γ-*p*-Dimethylaminocinnamoyl-β-*o*-hydroxyphenylpropane-*aa'*-dicarboxylic acid (HEILBRON, FORSTER, and WHITWORTH), 2166.

Dimethyl-2-homopiperonyl-6:7-dimethoxyhomophthalimide (HAWORTH, PERKIN, and PINK), 1720.

$C_{22}H_{24}O_{10}S$ Tetra-acetyl glucoside (CRAIK and MACBETH), 1639.

$C_{22}H_{28}O_4N_2$ Echitamine, and its salts (GOODSON and HENRY), 1640.

$C_{22}H_{37}O_2N_3$ Palmitaldehyde-*p*-nitrophenylhydrazone (STEPHEN), 1876.

22 IV

$C_{22}H_{17}O_2Cl_4Fe$ 7-Methoxy-4-phenylflavylium ferrichloride (ARMIT and ROBINSON), 1617.

$C_{22}H_{20}O_9N_3As$ 3''-Nitro-4''-anisoyl-3'-amino-4'-anisoyl-4-aminophenylarsinic acid (KING and MURCH), 2643.

$C_{22}H_{22}O_7N_3As$ 3''-Amino-4''-anisoyl-3'-amino-4'-anisoyl-4-aminophenylarsinic acid, and its salts (KING and MURCH), 2643.

$C_{22}H_{28}O_2N_2S_2$ 2:2'-Diacetylethylamino-5:5'-dimethyldiphenyl disulphide (CLARK), 974.

$C_{22}H_{28}O_4NCl$ Anhydro-7-demethylomethyl-ψ-corydaline, and its picrate (HAWORTH and PERKIN), 1462.

$C_{22}H_{28}O_4NI$ 7-Demethylo-ψ-corydaline methiodide (HAWORTH and PERKIN), 1460.

C_{23} Group.

$C_{23}H_{16}O_4$ Acetyl derivative of 7-hydroxy-2-phenyl*iso*flavone (BAKER and ROBINSON), 1985.

$C_{23}H_{18}O_{10}$ Datiscetin tetra-acetate (KALFF and ROBINSON), 1971.

$C_{23}H_{18}O_{11}$ Tetra-acetylquercetin (KUBOTA and PERKIN), 1894.

$C_{23}H_{22}O_{10}$ 3:3':4':5'-Tetramethylmyricetin diacetate (KALFF and ROBINSON), 183.

$C_{23}H_{22}O_{11}$ 2:4:6-Triacetoxy-3':4':5'-trimethoxybenzil (MARSH and STEPHEN), 1637.

$C_{23}H_{44}O_2$ *n*-Eicosanoylacetone, and its copper salt (MORGAN and HOLMES), 2896.

23 III

$C_{23}H_{15}O_2N$ 7:8-Methylenedioxy-11-phenylindenoquinoline, and its salts (ARMIT and ROBINSON), 1610.

$C_{23}H_{17}O_4Cl$ 4':5:7-Trihydroxy-2-phenyl-4-styrylbenzopyrylium chloride (WALKER and HEILBRON), 687.

$C_{23}H_{20}O_2N_2$ 2-*p*-Methoxyphenyl-3-*p*-methoxybenzylquinoxaline (MALKIN and ROBINSON), 376.

$C_{23}H_{20}O_3N_2$ Ethyl 3-keto-2:2-diphenyltetrahydroquinoxaline-4-carboxylate (INGOLD and WEAVER), 384.

Ethyl 4-keto-2:3:3-triphenyldimethylene-1:2-di-imine-1-carboxylate (INGOLD and WEAVER), 383.

$C_{23}H_{20}O_6S$ 7-Methoxy-4-phenylflavylium methohydroxide (ARMIT and ROBINSON), 1617.

$C_{23}H_{20}BrAs$ Phenylmesitylbenzylmethylarsonium bromide (HUNT and TURNER), 2669.

$C_{23}H_{21}O_3N_3$ Benzophenone-δ-4-carbethoxyphenylsemicarbazone (WILSON and CRAWFORD), 107.

$C_{23}H_{22}O_4N_2$ β-Phenyl-α-carbethoxyhydrazine-β-diphenylacetic acid (INGOLD and WEAVER), 383.

$C_{23}H_{23}O_4N$ 3-*p*-Dimethylaminophenyl-5-*o*-hydroxystyryl-Δ^5-*cyclo*hexen-1-one-2-carboxylic acid (HEILBRON, FORSTER, and WHITWORTH), 2164.

$C_{23}H_{24}O_2N_4$ *dl*-2′-Carboxybenzene-4-azodiphenyl-βγ-diamino-*n*-butanes, and their salts (MORGAN and SKINNER), 1739.

$C_{23}H_{24}O_6N_2$ *p*-Nitrobenzylbenzoyl-*l*-ecgonine, and its salts (GRAY), 1154.

$C_{23}H_{25}O_3N$ 3-(4′-Methoxy-2′-hydroxy)phenyl-5-*p*-dimethylaminostyryl-Δ^5-*cyclo*hexen-1-one (HEILBRON, FORSTER, and WHITWORTH), 2166.

$C_{23}H_{25}O_4N$ Benzylbenzoylecgonines, and their salts (GRAY), 1153, 1158.

$C_{23}H_{25}O_5N$ Benzyl-*o*-hydroxybenzoyl-*l*-ecgonine, and its picrate (GRAY), 1157.

o-Hydroxybenzylbenzoyl-*l*-ecgonine, and its salts (GRAY), 1155.

C_{24} Group.

$C_{24}H_{18}O_3$ 7-Methoxy-2-styryl*iso*flavone (BAKER and ROBINSON), 1986.

$C_{24}H_{16}O_4$ 7-Acetoxy-3-benzyl-2-phenylbenzo-γ-pyrone (BAKER), 2355.

$C_{24}H_{20}O_{11}$ Tetra-acetylquercetin methyl ether (KUBOTA and PERKIN), 1895.

$C_{24}H_{20}Ge$ Tetraphenylgermane (MORGAN and DREW), 1762.

$C_{24}H_{21}N$ Dibenzylquinaldine (MILLS and AKERS), 2477.

$C_{24}H_{22}O$ Benzylidenedibenzylacetone (MILLS and AKERS), 2477.

$C_{24}H_{22}N_2$ Substance, from 1-methyl-2-methylene-1:2-dihydro-β-naphthaquinoline and *p*-dimethylaminobenzaldehyde (MILLS and RAPER), 2472.

$C_{24}H_{42}O_{21}$ Maltodextrin-β (LING and NANJI), 645.

24 III

$C_{24}H_{16}OAs_2$ *oo*′-Diphenylylenearsenious oxide (AESCHLIMANN, LEES, MCCLELAND, and NICKLIN), 69.

$C_{24}H_{17}O_2N$ Anhydro-7:8-methylenedioxy-11-phenylindenoquinoline methohydroxide, and its salts (ARMIT and ROBINSON), 1611.

$C_{24}H_{19}O_4Cl$ 5:7-Dihydroxy-4′-methoxy-2-phenyl-4-styrylbenzopyrylium chloride (WALKER and HEILBRON), 687.

$C_{24}H_{25}O_4N$ Ethyl β-naphthylaminobenzylmalonates (WAYNE and COHEN), 455.

$C_{24}H_{26}O_9S_2$ Glyceryl tri-*p*-toluenesulphonate (FAIRBOURNE and FOSTER), 2762.

$C_{24}H_{27}O_4N$ Phenylethylbenzoylecgonines, and their salts (GRAY), 1155, 1158.

$C_{24}H_{27}O_5N$ Benzylhydroxymethylbenzoyl-*l*-ecgonines, and their picrates (GRAY), 1157.

$C_{24}H_{31}O_3N_3$ Ethyl 3-*p*-dimethylaminophenyl-5-methyl*cyclo*hexan-5-ol-1-one-2-carboxylate phenylhydrazone (HEILBRON, FORSTER, and WHITWORTH), 2165.

$C_{24}H_{41}O_2N_3$ Stearaldehyde *p*-nitrophenylhydrazone (STEPHEN), 1876.

C_{25} Group.

$C_{25}H_{18}O_6$ 7:8-Diacetoxy-2:3-diphenylbenzo-γ-pyrone (BAKER), 2357.

$C_{25}H_{20}O$ Phenyl-α-naphthylmethyl *p*-tolyl ketone (MCKENZIE and TATTERSALL), 2529.

$C_{25}H_{22}O$ αβ-Diphenyl-α(α-naphthyl)-propan-β-ol (MCKENZIE and TATTERSALL), 2527.

$C_{25}H_{24}N_2$ Substance, from 1-ethyl-2-methylene-1:2-dihydro-β-naphthaquinoline and *p*-dimethylaminobenzaldehyde (MILLS and RAPER), 2472.

25 III

$C_{25}H_{19}O_4Cl$ 4′:4″:7-Trihydroxy-2:4-distyrylbenzopyrylium chloride (HEILBRON, WALKER, and BUCK), 694.

$C_{25}H_{21}O_4Cl$ 5:7-Dimethoxy-2′- and -4′-hydroxy-2-phenyl-4-styrylbenzopyrylium chloride (WALKER and HEILBRON), 688.

$C_{25}H_{22}O_4N_2$ Ethyl acetyl-3-keto-2:2-diphenyltetrahydroquinoxaline-4-carboxylate (INGOLD and WEAVER), 384.

$C_{25}H_{24}NI$ Dibenzylquinaldine methiodide (MILLS and AKERS), 2477.

$C_{25}H_{25}N_2I$ Substance, from β-naphthaquinaldine ethiodide and *p*-dimethylaminobenzaldehyde (MILLS and RAPER), 2472.

$C_{25}H_{27}O_4N$ Ethyl 3-*p*-dimethylaminophenyl-5-*o*-hydroxystyryl-Δ^5-*cyclo*hexen-1-one-2-carboxylate (HEILBRON, FORSTER, and WHITWORTH), 2163.

$C_{25}H_{29}O_4N$ Phenyl-*n*-propylbenzoyl-*l*-ecgonine, and its hydrochloride (GRAY), 1156.

$C_{25}H_{29}O_5N$ Benzyltropoyl-*l*-ecgonine, and its salts (GRAY), 1156.

25 IV

$C_{25}H_{32}O_3NCl$ 5:7-Dihydroxy-4′-dimethylamino-2-phenyl-4-styrylbenzopyrylium chloride, and its salts (WALKER and HEILBRON), 687.

C_{26} Group.

$C_{26}H_{20}O_6$ 5:7-Diacetoxy-3-benzyl-2-phenylbenzo-γ-pyrones (BAKER), 2356.

$C_{26}H_{22}N_4$ Benzaldehydediphenylene-4:4′-dihydrazone (CHATTAWAY, IRELAND, and WALKER), 1853.

$C_{26}H_{50}O_6$ Acid, and its salts, from saponification of cutin (LEGG and WHEELER), 1419.

26 III

$C_{26}H_{16}N_4Br_4$ 1:4-Di(2:4-dibromophenyl)-3:6-diphenyl-1:4-dihydro-1:2:4:5-tetrazine (CHATTAWAY and WALKER), 983.

$C_{26}H_{19}O_6Cl$ Trihydroxymethylenedioxy-2:4-distyrylbenzopyrylium chlorides (HEILBRON, WALKER, and BUCK), 696.

$C_{26}H_{20}O_4N_6$ Nitrobenzaldehydediphenylene-4:4′-dihydrazones (CHATTAWAY, IRELAND, and WALKER), 1854.

$C_{26}H_{21}O_4Cl$ Dihydroxymethoxy-2:4-distyrylbenzopyrylium chlorides (HEILBRON, WALKER, and BUCK), 695.

$C_{26}H_{21}O_5Cl$ Trihydroxymethoxy-2:4-distyrylbenzopyrylium chlorides (HEILBRON, WALKER, and BUCK), 695.

$C_{26}H_{23}O_5Cl$ 3′:5:7-Trimethoxy-4′-hydroxy-2-phenyl-4-styrylbenzopyrylium chloride (WALKER and HEILBRON), 689.

$C_{26}H_{24}O_4N_2$ *Py-N*-Methylphenyldiveratro*iso*harmyrine (ARMIT and ROBINSON), 1613.

$C_{26}H_{26}NI$ Dibenzylquinaldine ethiodide (MILLS and RAPER), 2473.

$C_{26}H_{29}O_4N$ Ethyl *p*-dimethylamino-*o*-methoxystyryl-Δ^5-*cyclo*hexen-1-one-2-carboxylates (HEILBRON, FORSTER, and WHITWORTH), 2164.

$C_{26}H_{29}O_5N$ Ethyl 3-*p*-dimethylaminophenyl-5-(methoxy-2′-hydroxy)styryl-Δ^5-*cyclo*hexen-1-one-2-carboxylates (HEILBRON, FORSTER, and WHITWORTH), 2165.

$C_{26}H_{32}O_6N_2$ Diacetylechitamine, hydrochloride of (GOODSON and HENRY), 1645.

$C_{26}H_{32}O_6N_4$ Ethyl 6:6-diphenylhexahydro-1:2:3:4-tetrazine-1:2:3:4-tetracarboxylate (INGOLD and WEAVER), 386.

26 IV

$C_{26}H_{22}O_4N_4As_2$ 3′-Amino-4′-hydroxybenzoyl-4-aminoarsenobenzene (KING and MURCH), 2650.

C_{27} Group.

$C_{27}H_{18}N_2$ 5:6-(2:3-Diphenylindolo) (6:7)-quinoline (ARMIT and ROBINSON), 1615.

$C_{27}H_{22}O_{14}$ Myricetin, synthesis of (KALFF and ROBINSON), 181.

$C_{27}H_{46}O$ Cholesterol, molecular weight of (PARTINGTON and TWEEDY), 496.

27 III

$C_{27}H_{21}O_6Cl$ 4″:7-Dihydroxy-3″-methoxy-3′:4′-methylenedioxy-2:4-distyrylbenzopyrylium chloride (HEILBRON, WALKER, and BUCK), 696.

$C_{27}H_{23}O_4Cl$ 7-Hydroxy-4′:4″-dimethoxy-2:4-distyrylbenzopyrylium chloride (HEILBRON, WALKER, and BUCK), 694.

$C_{27}H_{26}O_3NCl$ 5:7-Dimethoxy-4′-dimethylamino-2-phenyl-4-styrylbenzopyrylium chloride, and its ferrichloride (WALKER and HEILBRON), 689.

$C_{27}H_{31}O_4N$ Ethyl 1-methoxy-3-*o*-methoxyphenyl-5-*p*-dimethylaminostyryl-$\Delta^{1:5}$-*cyclo*hexadiene-2-carboxylate (HEILBRON, FORSTER, and WHITWORTH), 2165.

$C_{27}H_{32}O_3N_2$ Ethyl 3-*p*-dimethylaminophenyl-5-*p*-dimethylaminostyryl-Δ^5-*cyclo*-hexen-1-one-2-carboxylate (HEILBRON, FORSTER, and WHITWORTH), 2165.

C_{28} Group.

$C_{28}H_{16}O$ Dianthranyl oxide (COOKE, HEILBRON, and WALKER), 2253.

$C_{28}H_{16}S_2$ Dianthranyl disulphide (COOKE, HEILBRON, and WALKER), 2252.

$C_{28}H_{16}S_4$ Dianthranyl tetrasulphide (COOKE, HEILBRON, and WALKER), 2254.

$C_{28}H_{20}O$ Phenyl-α-naphthylacetonaphthone (MCKENZIE and TATTERSALL), 2529.

28 III

$C_{28}H_{22}O_3N_2$ 2-Keto-3:3:4-triphenyl-1-*p*-nitrobenzyltrimethyleneimine (INGOLD and WEAVER), 386.

$C_{28}H_{24}O_2N_6$ Benzildi-δ-phenylsemicarbazone (HOPPER), 1288.

$C_{28}H_{26}O_2N_4$ Anisaldehydediphenylene-4:4′-dihydrazone (CHATTAWAY, IRELAND, and WALKER), 1853.

$C_{28}H_{27}O_2N$ *p*-Dimethylaminotetraphenylethylene glycol (SINGH), 2446.

$C_{28}H_{27}N_2I$ 6-Methyl-1:1′-diethylcarbocyanine iodide (MILLS and RAPER), 2474.

28 IV

$C_{28}H_{24}O_2N_2S_2$ 2:2′-Dibenzoylmethylaminodiphenyl disulphide (CLARK), 975.

$C_{28}H_{26}O_3NCl$ 7-Hydroxy-4′-methoxy-4″-dimethylamino-2:4-distyrylbenzopyrylium chloride (HEILBRON, WALKER, and BUCK), 695.

$C_{28}H_{28}O_6N_6S_2$ Di-4′-sulphobenzenedis-4-azodiphenyl-βγ-diamino-*n*-butanes, and their salts (MORGAN and SKINNER), 1735.

C_{29} Group.

$C_{29}H_{28}$ Tetrabenzylmethane (TROTMAN), 94.

29 II

$C_{29}H_{23}N$ 1-Methyltetraphenylpyrrole (PERKIN and PLANT), 1141.

29 III

$C_{29}H_{27}N_2Br$ 5:6-Benzo-1:1′-diethylcarbocyanine bromide (MILLS and RAPER) 2474.

29 IV

$C_{29}H_{28}O_{11}N_4As_2$ 3′-Amino-4′-anisoyl-4-aminophenylarsinic acid *s*-carbamide (KING and MURCH), 2643.

29 V

$C_{29}H_{43}O_6NBrS$ *d*-4-Phenyl-4′-carbethoxybispiperidinium-1:1′-spiran bromocamphorsulphonates (MILLS and WARREN), 2512.

C_{30} Group.

$C_{30}H_{20}O_4$ Dimethoxydianthraquinone (PERKIN and YODA), 1887.
$C_{30}H_{44}O_4$ Menthyl benzylidenemalonate (WAYNE and COHEN), 459.

30 III

$C_{30}H_{28}O_2N_6$ Benzildibenzylsemicarbazone (HOPPER), 1286.

30 IV

$C_{30}H_{28}N_4Br_6S_2$ 1-Toluidino-methylbenzthiazole tribromides (HUNTER), 2026.
$C_{30}H_{30}N_4Br_8S_2$ 1-*m*-Toluidino-*m*-toluthiazole tribromide hydrobromide (HUNTER) 2028.

C_{31} Group.

$C_{31}H_{32}ON_2$ Di-*p*-dimethylaminobenzhydryl ketone (SINGH), 2447.

C_{32} Group.

$C_{32}H_{34}$ $\alpha\delta$-Diphenyl-$\beta\gamma$-dibenzyl-$\beta\gamma$-dimethylbutane (TROTMAN), 92.
α-Phenyl-$\beta\beta$-dibenzylpropane (TROTMAN), 93.

32 II

$C_{32}H_{16}O_6$ Diacetoxynaphthadianthrone (PERKIN and YODA), 1886.
$C_{32}H_{20}O_6$ 3:6′-Diacetoxydianthraquinone (PERKIN and YODA), 1886.
$C_{32}H_{22}O_4$ 7-Cinnamoyloxy-2-styryl*iso*flavone (BAKER and ROBINSON), 1986.

32 III

$C_{32}H_{28}O_6N_2$ Anhydro-α-diphenylacetyl-α(or β)-carboxy-β(or α)-carbethoxyhydrazine-β-diphenylacetic acid (INGOLD and WEAVER), 382.

C_{33} Group.

$C_{33}H_{30}O_9$ Rottlerin, preparation of (DUTT), 2046.

C_{34} Group.

$C_{34}H_{30}O_6N_2$ Ethyl 3:5-diketo-4:4:6:6-tetraphenylhexahydropyridazine-1:2-dicarboxylate (INGOLD and WEAVER), 382.

C_{36} Group.

$C_{36}H_{26}N_4$ Cinnamaldehydediphenylene-4:4′-dihydrazone (CHATTAWAY, IRELAND, and WALKER), 1853.
$C_{36}H_{30}Ge_2$ Hexaphenyldigermane (MORGAN and DREW), 1764.
$C_{36}H_{62}O_{31}$ Maltodextrin-α (LING and NANJI), 645.

36 III

$C_{36}H_{30}OGe_2$ Triphenylgermanium oxide (MORGAN and DREW), 1763.
$C_{36}H_{51}O_4N$ Menthyl β-anilinobenzylmalonate (WAYNE and COHEN), 459.

C_{38} Group.

$C_{38}H_{76}O_2$ Dioctadecylacetic acid (ADAM and DYER), 71.

C_{39} Group.

$C_{39}H_{42}O_9$ Methoxyrottlerin (DUTT), 2047.
$C_{39}H_{76}O_4$ Dioctadecylmalonic acid (ADAM and DYER), 71.

C_{41} Group.

$C_{41}H_{40}O_{16}$ Lignol (POWELL and WHITTAKER), 134.
$C_{41}H_{44}O_{10}$ Acetylmethoxyrottlerin (DUTT), 2047.

41 III

$C_{41}H_{44}O_{10}Br_2$ Dibromoacetylmethoxyrottlerin (DUTT), 2047.

C_{44} Group.

$C_{44}H_{24}O_6$ Dibenzoyldihydroxydianthraquinone (PERKIN and YODA), 1887.

C_{47} Group.

$C_{47}H_{44}O_{16}$ Acetylrottlerin (DUTT), 2046.

47 III

$C_{47}H_{44}O_{19}Br_2$ Dibromoacetylrottlerin (DUTT), 2047.

C_{48} Group.

$C_{48}H_{40}O_4Ge_4$ Tetra-anhydrotetrakisdiphenylgermanediol (MORGAN and DREW), 1766.

$C_{48}H_{42}O_5Ge_4$ Trianhydrotetrakisdiphenylgermanediol (MORGAN and DREW), 1766.

C_{51} Group.

$C_{51}H_{57}O_6Al$ Aluminium benzoylcamphor, and its mutarotation (FAULKNER and LOWRY), 1082.

C_{56} Group.

$C_{56}H_{28}Br_2S_2$ *ms*-Dibromodiheptacyclene disulphide (COOKE, HEILBRON, and WALKER), 2254.

C_{75} Group.

$C_{75}H_{44}O_{15}$ Benzoylrottlerin (DUTT), 2047.

ERRATA.

VOL. 115 (1919).

Page	Line	
376	17	*for* "207°" *read* "175°."

VOL. 123 (1923).

2455	13*	*for* "**40, 454**" *read* "**41, 545.**"
,,	1*	*for* "610" *read* "510."
2456	2	*for* "**42, 930**" *read* "**45, 261.**"

VOL. 127 (1925).

264	6	*for* "7·5" *read* "7·64."
,,	19	
,,	10	*for* "7·50" *read* "7·64."
,,	21	*for* "0·996" *read* "1·01."
,,	30	

* From bottom.

Vol. 127 (1925).

Page	Line	
268	17	*for* "(I′)" *read* "free iodine (I)"
„	18 to 34	*replace by* "From the above data we obtain for the composition of the dark equilibrium mixture: $I' = 0{\cdot}02237$ gm.-ion per litre. $I_2 = 0{\cdot}00174$ gm.-mol. per litre. $I_2' = 0{\cdot}00638$ gm.-ion per litre. Whence we obtain $K = \frac{(1{\cdot}625 \times 10^{-2})(0{\cdot}00174)^{\frac{1}{2}}}{(0{\cdot}380 \times 10^{-2})(0{\cdot}02237)} = 7{\cdot}97$, a value much lower than those obtained by Maitland or Brönsted."
269	9	*for* "$K = 23{\cdot}6$" *read* "$K = 7{\cdot}97$."
284	11	*for* "CO_2Ph" *read* "CO_2Et."
305	3*	*for* "*Low-melting*" read "*High-melting.*"
722		Invert Fig. 1.
917	9*	atomic number of tungsten, *for* "76" *read* "74."
936	17*	*for* "Grafton" *read* "Albemarle."
944	footnote	*for* "£75" *read* "£175."
945	1*	*for* "based" *read* "placed."
1456	17	for "*ketonor-7-demethylo-ψ-corydaline*" read "*keto-7-demethylo-ψ-corydaline.*"
1461	10	*for* "XIII" *read* "XII."
1543	16 & 19	*for* "naphtholbenzoin" *read* "naphtholbenzein."
1745	Formula III.	Place "---" before "NMe."
1750	7	*for* "(IX)" *read* "(X)."
„	8	*add* "$CH_2{=}C(CO_2Et)_2$ (X.)"
„	12	*add* "The correct arrangement is (IX)."
1819	12*	*after* "was" *insert* "converted into hydrochlorides and."
1820	6*	*before* "of" *insert* "mainly."
2403	Fig. 3	(ordinates) *for* "0, 10, 20, 30, 40" *read* "10, 20, 30, 40, 50."
2435	3	for "*Pyridine*" read "*Nicotine.*"

* From bottom.

Vol. 127 (Trans., 1925).

Page	Line	
2997	3*	col. ii *insert* "[with *Frederick J.* **Corby**, *Oliver C.* **Elvins**, *Evelin* **Jones**, *Richard E.* **Kellett**, and *Cyril J. A.* **Taylor**]."

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,, ,, ,, ,, (Single Parts)	per part	5 0	7 6
Journal, 1862—1895	per ann.	1 10 0	1 10 0
,, ,, ,, (Single Parts)	per part	2 6	2 6
,, 1896—1914	per ann.	2 0 0	2 0 0
,, ,, ,, (Single Parts)	per part	3 6	3 6
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,, ,, ,, ,, (Single Parts)	per part	3 0	4 0
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,, ,, ,, ,, ,, (Single Parts)	per part	3 0	4 0
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,, ,, ,, ,, ,, (Single Parts) (Issued by the Bureau of Chemical Abstracts)	per part	4 9	6 6
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*Proceedings, 1885—1914	per vol.	7 6	7 6
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,, ,, ,, III. 1883—1892	per vol.	7 6	7 6
,, ,, ,, IV. 1893—1902	per vol.	10 0	10 0
,, ,, ,, V. 1903—1912	per vol.	2 0 0	2 10 0
,, ,, ,, VI. 1913—1922	per vol.	3 5 0	5 0 0
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,, ,, Vol. II. 1901–1913		7 0	8 0
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* *Included with Journal as from January*, 1915.

† *As from January* 1924, *the Abstracts were separated from the Transactions and were published independently.*

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